JOURNAL OF ANALYTICAL CHEMISTRY
VOLUME 8 NUMBER 3 1953

# THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Number 3

Volume VIII, 1953

(MAY - JUNE)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R. IN ENGLISH TRANSLATION

May-June, 1953

TABLE OF CONTENTS


| | | Page | Russ. page |
|---|---|---|---|
| 1. | High Frequency Titration. O. L. Kaptsan and V. A. Teplyakov. | 151 | 131 |
| 2. | The Use of Dithizone as an Extraction Indicator. A. G. Karabash | 159 | 140 |
| 3. | Thermal Analysis with Registration of the Volume of Gas Evolved. B. Ya. Teitelbaum and L. G. Berg. | 171 | 152 |
| 4. | Determination of Carbon and Hydrogen in Organic Compounds Containing Sulfur and Nitrogen, in the Presence of Catalysts. P. N. Fedoseev and M. M. Pavlenko | 175 | 158 |
| 5. | The Behavior of Certain Cations During the Complexometric Determination of Water Hardness. T. B. Styunkel, E. M. Yakimets, and D. A. Savinovsky. | 179 | 163 |
| 6. | Microcrystalloscopic Reactions for Cyanides. L. M. Korenman and A. A. Belyakov | 185 | 168 |
| 7. | The Analytical Use of Potassium Manganate Hydrolysis. S. F. Zavgorodny. | 189 | 172 |
| 8. | A Comparative Evaluation of Qualitative Reactions for Bismuth Carried out by Trituration. E. P. Ozhigov | 193 | 175 |
| 9. | Determination of Vapors of Fluoorganic Compounds in Air. E. A. Peregud and B. S. Boikina. | 197 | 178 |
| 10. | p-Anisidine — A Sensitive Reagent for Cupric Cations. A. Kh. Batalin | 201 | 182 |
| 11. | Determination of Indicator Error by the Korenman Method from the Weight of the Substance. L. L. Teodorovich | 203 | 184 |

Criticism

| | | | |
|---|---|---|---|
| 12. | Reply to A.K. Babko's Criticisms of the Article "The Quantitative Determination of Trivalent Iron with Tetraborate." (J. Anal. Chem., 7, 280, 1952). | | |

Chronicle

| | | | |
|---|---|---|---|
| 13. | Yu. A. Chernikov. | 209 | 188 |
| 14. | Ukrainian Conference on Chemical Control in the Metallurgical and Metal-Working Industries. | 211 | 190 |

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R.

Volume VIII, No. 3

May-June, 1953

(A Publication of the Academy of Sciences of the U.S.S.R.)

---

IN ENGLISH TRANSLATION

Copyright, 1954

CONSULTANTS BUREAU

152 West 42nd Street, New York 18, N.Y.

Printed in Great Britain

Annual subscription $80.00
Single issue 20.00

Note: The sale of photostatic copies of any portion of this copyrighted translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue can be purchased from the publisher for $7.50.

# HIGH FREQUENCY TITRATION

O. L. Kaptsan and V. A. Teplyakov

Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow

## I

Many articles appeared in recent years which have been devoted to a new volumetric method – the method of high frequency titration (at current frequencies of the order of megacycles). This method is essentially the same as conductometric titration, but in contrast to the latter, observations of changes in the electrical characteristics of the solution during high frequency titration (H.F. titration) are made by enclosing the vessel containing the titration solution within the current circuit, so that there is no need for electrodes to be placed inside the solution, instead, they are placed outside the vessel in direct contact with the walls (external electrodes). By means of this method which is also very accurate, it is possible to widen the scope of volumetric analysis.

Just like conductometric titration, H. F. titration is possible because the electrical resistance of a solution varies with the electrolyte in solution and with the concentration of the electrolyte. However, during H.F. titration in contrast to the usual conductometric titrations, the changes in the capacity component of the total electrolyte resistance are also of essential significance. For H.F. titrations the electrodes are placed outside the vessel since the resistance of the vessel itself does not present an essential barrier to the passage of the current at the frequencies employed.

Changes in the resistance and capacity of the dielectric-viz., the solution with changing composition – are measured by methods normally used in radio-technics. A detailed analysis of the apparatus described in the literature for H.F. titration will be given below.

A large number of articles has been devoted to the application of H.F. titration in analysis, which include reviews such as those of Blake [1], Blaedel and Malmstadt [2], and Hall [3]. A systematic review of H.F. titrations appears in the German journal of analytical chemistry [4,5].

In addition to H.F. titration itself, which is discussed below in detail, H. F. methods have already found a variety of uses. Thus, long before the appearance of foreign papers on this question, Troitsky [6], used measurements of the dielectric constants obtained by means of a H.F. generator for separating the adsorption zones of colorless compounds during chromatographic analysis. Other papers have been devoted to the same purpose [7,8]. By means of a H.F. generator it is possible to determine the percentage of water in alcohol in a matter of seconds with an accuracy of $\pm$0.05% for a 1% weight concentration of water [9]. A change in the concentration of KCl in benzene can be determined for concentrations of the order of 0.0006% [10]. H.F. set-ups have been used for studying the kinetics of chemical reactions in solutions [11,12], and for investigating metallic complex salts [13]. The measurement of the dielectric constants by means of H.F. was used by the Soviet radio amateur Velichko [16], for an important practical purpose – the rapid determination of grain moisture.

The application of H. F. apparatus for titration is of comparatively recent origin [15,10]. It has been shown that the accuracy of H.F. titrations in most cases is not less than, and in many cases exceeds that of usual analytical methods. Thus, normal acid-base titration can be carried out using a H.F. generator in 3-4 minutes, with the same accuracy [15,16,17, et al] as the potentiometric titration method. Weak acids with dissociation constants of the order of $10^{-7}$ [18], can be titrated with a fair degree of accuracy

By means of a 350-megacycle generator it was found possible to titrate silver nitrate with 0.1 M sodium chloride when the total concentration of electrolyte consisted of 10 mole % of silver nitrate and 90 mole % sodium nitrate at the beginning of titration [19]. The total concentration of electrolyte at the end was equivalent to 0.2 M approximately. Normal conductometric titration would be impossible in practice if such an amount of an inert electrolyte ($NaNO_3$) was present. The titration curves for this case are shown in Fig. 1. Readings of the registering instrument are plotted along the ordinate, against the amount of reagent added in mls along the abscissa. The Fig. shows that all the points lie on two straight lines intersecting at a point which corresponds to the end point. In the same article titration curves for mercuric nitrate with potassium thiocyanate, and of oxalic acid with thorium nitrate are also given. The error in each case does not exceed 0.2%.

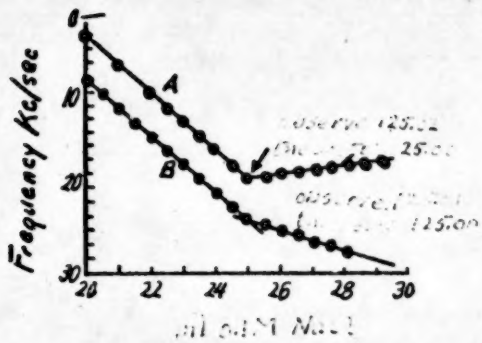



Fig. 1.

H.F. titration enables small amounts of thorium to be determined in the presence of zirconium and titanium with an error of not more than ±1.2% [20], and enables water hardness to be determined [21], with results for the calcium content which are better than those obtained by the standard method used in America. The chloride ion can be determined with a high degree of accuracy (an error of only 0.2%) by precipitation with mercury salts in 0.00004-0.003 M HCl [22]; the error of a potentiometric method for such a system is 2%, while that of the conductometric method is 1.5%. H.F. titration gives good results for the determination of sulfur in sea water and in gasoline products. 0.01-0.0001 N $SO_4^{2-}$ solutions can be titrated in the presence of $H_2O_2$ with an error of ± 2.2% [23]. (0.09–6.72 mg of sulfur can be determined). H.F. generators with frequencies of 20 megacycles can be used for the volumetric titration of beryllium with ammonium phosphate, NaOH, or ammonium hydroxide [24]. The error for the determination of 10-40 mg of beryllium in the presence of excess HCl is on an average equal to ±0.7%. There was no satisfactory method for the volumetric determination of beryllium before the advent of the H.F. method.

In addition to the neutralization and precipitation reactions described, H.F. analysis can also be used for oxidation-reduction titrations [10 2], and for reactions accompanied by the formation of soluble complexes.

From the review given above it is clear that H.F. titrations can give analytical results on a par with gravimetric methods (0.0 n %) and sometimes better than the latter. Another advantage of the new method of titration is its speed, which depends only on the velocity of the reaction used for analysis in solution, and the good reproducibility of the results.

The general form of the curve obtained during H.F. titration is reminiscent of those obtained during conductometric titration. (See Fig. 1). The curves obtained during H.F. titration are usually linear near the equivalence point, nevertheless, even when there are deviations from linearity, they do not lower the accuracy of the method.

It has been suggested recently that in cases where the final end point is not very clearly defined during H.F. titration, a differential method could be used [25]. When this method is used, the reagent is added to the solution being titrated at a constant rate. The apparatus automatically registers both the direct changes in the electrical characteristics of the solution during the titration process (the frequency changes) and the velocity with which they change (i.e. the change of frequency in unit time). The differential method gives a sharper end point so that, e.g. even small amounts of $CO_3^{2-}$ can be detected in NaOH.

The method described, however, has its limitations. The main drawback is the total concentration of the titrated solution. The maximum sensitivity of the H.F. titration method will depend both on the

nature of the coupling between the titration vessel and the generator circuit (this will be considered in detail below) and on the composition of the solution. Thus, for H.F. titration with a 30 megacycle generator (by the beat method) the maximum sensitivity for the determination of HCl concentration in solution is given for concentrations of HCl of the order of 0.003 N, while for sodium chloride the maximum sensitivity is given for concentrations of 0.014 N [2, 26]. In this range the change in concentration can be determined with an accuracy of 0.05%. If titration is carried out in which measurements of current of voltage are involved, then working at the same frequency and with the same apparatus there are two regions of maximum sensitivity: for sodium chloride these are $-0.0005-0.01$ N and $0.05-1.0$ N. Here the changes in sodium chloride concentration can be determined with an accuracy of 0.5%. The greater the equivalent conductivity of the solution, the narrower the concentration range (thus, the range is narrower for HCl than for NaCl). Nevertheless, titrations are very often carried out in analytical chemistry where the electrolyte concentration exceeds 1 M. When solutions of higher concentration are titrated, it becomes necessary to increase the frequency of the current used for titration. In particular, it was for concentrations of the order of about 1 M that a H.F. apparatus operating at 350 megacycles was constructed [19].

## II

It has already been stated that it is the changes in the electrical characteristics of the solution with changes in concentration that are used in H.F. titrations.

Any solution considered as a dielectric can be characterized by three independent constants: 1) the dielectric permeability ($\epsilon$); 2) the magnetic permeability ($\mu$) which is practically constant for solutions of electrolytes, and 3) the specific conductivity or specific resistance which is determined by the value of the total H.F. losses in the dielectric. For electrolytes, the specific resistance and the dielectric constant at radio frequencies depend on the concentration of the solution and on the current frequency [27].

In order that in our review of the methods proposed in the literature we may differentiate that which is characteristic for and on which H.F. titration is based from the usual radio technical set ups [28] which are not specific in the given instance, we shall introduce the concept of the "electric cell" (donor).

Thus, any H.F. titration apparatus consists of an electric cell and a measuring set up, the chief component of which is the H.F. generator.

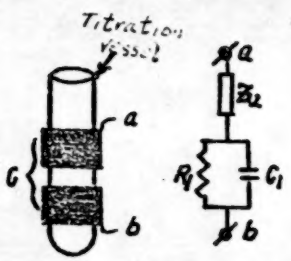



Fig. 2.

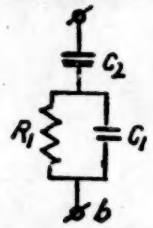



Fig. 3.

Electrical cells of type "C". If a vessel containing an electrolyte is placed in a H.F. field, e.g. in a condenser, then the equivalent electrical circuit of the cell may be represented as shown in Fig. 2 [3]. Here $R_1$ and $C_1$ are the resistance and capacity of the electrolyte itself, respectively, while $Z_x$ is the total resistance of the condenser, the plates of which are formed on the one hand by the electrodes, and on the other by the surface of the liquid at the vessel walls, the walls of the vessel acting in this case as the dielectric. Resistance $R_1$ and capacity $C_1$ are proportional to the specific resistance and the dielectric permeability of the electrolyte, these in turn depend on the geometrical dimensions of the vessel and the condenser plates and also on the concentration and the nature of the solution. $R_1$ and $C_1$ could be determined directly, if the condenser plates were arranged on the inside surfaces of the vessel walls, i.e., if the plates were in contact with the electrolyte. At the frequencies used in H.F. titration however $R_1$ and $C_1$ differ from the $R_1$ and $C_1$ obtained for the same solutions when D.C. or low frequency A.C. are used, because of a decrease in relaxation force with increasing frequency [27]. During titration, the frequency changes only insignificantly within limits such that $R_1$ and $C_1$ for a given solution are practically independent of frequency changes. $Z_x$ can be measured by any of the methods used for measuring small capacities with low losses, e.g., by means of a Q-meter, the inner

surface of the vessel walls having been preliminarily covered with a silver layer or the vessel filled with mercury. At the frequencies employed in H.F. titration the losses in the glass of the titration vessel can be neglected. Therefore the equivalent circuit Fig. 2 can be simplified [26,29 30]. The simplified circuit is shown in Fig.3.

Only the terminals ab (Fig.3) are accessible for measurement during H.F. titration. Having measured the total resistance Z of the circuit over the terminals ab, we can determine the values of $R_1$ and $C_1$. During H.F. titration it is not the absolute values of the resistances $R_1$ and capacity $C_1$ that are determined, but the way in which the total resistance of the circuit Z changes with the concentration changes of the solution. It is important therefore that changes in $R_1$ and $C_1$ should effect the strongest possible changes in the total resistance Z, so that it is essential to choose the correct ratio between the resistance of capacity $C_2$ and the total resistance of branch $R_1C_1$.

The total resistance of the circuit shown in Fig.3 will be:

$$Z = \frac{1}{j\omega C_2} + \frac{1}{\frac{1}{R_1} + j\omega C_1} = \frac{R_1}{1 + (\omega C_1 R_1)^2} - j\left[\frac{\omega C_1 R_1^2}{1 + (\omega C_1 R_1)^2} + \frac{1}{\omega C_2}\right], \quad (1)$$

where $\omega = 2\pi f$, the angular frequency (f = the current frequency).

From this formula it is clear that the active component of the total resistance

$$R = \frac{R_1}{1 + (\omega C_1 R_1)^2} \quad (2)$$

which is most strongly dependent on changes in $R_1$, when

$$(\omega C_1 R_1)^2 \ll 1. \quad (3)$$

When

$$(\omega C_1 R_1)^2 \gg 1, \quad (4)$$

R is strongly dependent not only on $R_1$ but also on $C_1$.

When condition (3) is satisfied the reactive component of the total resistance

$$X = \frac{\omega C_1 R_1^2}{1 + (\omega C_1 R_1)^2} + \frac{1}{\omega C_2} \quad (5)$$

will be most strongly dependent on $R_1$ and $C_1$. When condition (4) is satisfied X depends only on $C_1$.

In practice it can happen that during titration $R_1$ decreases while $C_1$ increases, or vice-versa. In such a case it is only necessary that conditions (3) and (4) be satisfied where R depends only on $R_1$, while X depends only on $C_1$. In this case non-fulfilment of the given conditions will decrease the sensitivity of titration. Conditions (3) and (4) can be fulfilled by choosing the operating frequency $\omega$ and the value of the condenser C.

Electrical cells of type "C" have been used in a number of investigations using H.F. titration (see e.g. [1,16,31,32]).

Electrical cells of type "L". In the previous section dealing with the equivalent circuits for C-cells we developed to some extent the theories re cells of this type already current in the literature [3,25,26,30,31]. No analysis of the L-type cell has hitherto been given, and no equivalent circuits of a coil with a suitable vessel for titration have been given anywhere.

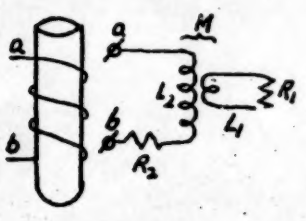



Fig. 4.

An "L" type cell is characterized by the fact that the vessel containing the electrolyte is made the core of a H.F. self induction coil. The simplified equivalent circuit for this case is given in Fig. 4. Here $L_2$ is the inductance and $R_2$ is the resistance of a coil when the titration vessel containing no electrolyte is placed in it. $L_1$ and $R_1$ are the corresponding inductance and resistance which are characteristic of the solution.

For a given frequency the inductance $L$ is determined only by the geometrical dimensions of the titration vessel; it increases with increase in the ratio $D/l$ where D is the diameter of the vessel and $l$ - the height to which it is filled with electrolyte at that part which is located in the high frequency field of the coil; $R_1$ – is proportional to the specific resistance of the electrolyte; $L_1$ and $L_2$ are the mutual inductances where the coefficient of mutual inductance is $M = k\sqrt{L_1 L_2}$ where $k$ is the coupling coefficient; $k$ is greater the greater the volume of coil occupied by electrolyte; $k$ is always less than one.

The circuit in Fig. 4 can be transformed into the circuit shown in Fig. 5.

In this circuit $L_{int.}$ and $R_{int.}$ are the inductance and resistance introduced into the coil circuit when the titration vessel is filled with electrolyte. From the theory of coupled circuits [33], it is known that the resistances introduced are determined by the following formulas :

$$R_{int.} = \frac{\omega^2 M^2}{R_1^2 + \omega^2 L_1^2} R_1 = \frac{k^2 \omega L_2}{1 + \left(\frac{R_1}{\omega L_1}\right)^2} \left(\frac{R_1}{\omega L_1}\right). \tag{6}$$

$$L_{int.} = -\frac{\omega^2 M^2}{R_1^2 + \omega^2 L_1^2} L_1 = -\frac{k^2 L_2}{1 + \left(\frac{R_1}{\omega L_1}\right)^2} \tag{7}$$

Let us introduce the dimensionless quantity $Q = \frac{\omega L_1}{R_1}$ by which we shall characterize the solution in future.

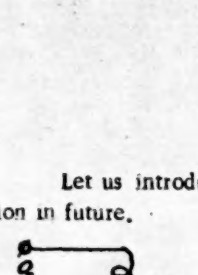



Fig. 5

The physical meaning of the quantity Q which is called the quality can be made clear by means of the following considerations: let us multiply both the numerator and denominator of the expression for Q by $I_m^2/2$ and substitute $(2\pi/T)$ for $\omega$. Here $I_m$ is the amplitude of the H.F. current, while $T$ is the period of the H.F. oscillation. Then

$$Q = \frac{2\pi \frac{LI_m^2}{2}}{\frac{RI_m^2}{2} T}$$

i.e. the quality is directly proportional to the amplitude value of the energy in the coil and is inversely proportional to the energy loss in the coil for one period at high frequency. By characterizing the solution by the value $Q_1$ it is possible to express $R_{int.}$ and $L_{int.}$ in terms of $Q$.

$$R_{int.} = \frac{k^2 \omega L_2}{1 + Q_1^2} Q_1 \tag{8}$$

$$L_{int.} = -\frac{k^2 L_2 Q_1^2}{1 + Q_1^2}. \tag{9}$$

The quality of the coil without any electrolyte in the titration vessel will be $Q_2 = \frac{\omega L_2}{R_2}$, and with electrolyte

$$Q_1 = \frac{\omega(L_2 + L_{int.})}{R_2 + R_{int.}} = Q_2 \frac{1 + Q_1^2(1 - k^2)}{1 + Q_1^2 \; 1 + \left(\frac{k^2 Q_2}{Q_1}\right)} \tag{10}$$

The value of $k$ which depends on the geometrical dimensions of the coil and the titration vessel can be determined easily by means of a simple experiment. If the inner surface of the vessel is silvered then $Q_1$ will be so much greater than unity that it may be accepted that $Q_1^2 \gg 1$, when

$$L_{int.} = -\frac{k^2 L_2}{1 + \frac{1}{Q_1^2}} \approx -k^2 L_2. \tag{11}$$

Thus, having measured the inductance $L_1'$ of the coil containing a silvered titration vessel and the inductance $L_2$ of the coil with a vessel which has not been silvered, we can find the coupling coefficient:

$$k = \sqrt{\frac{L_2 - L_1'}{L_2}} = \sqrt{1 - \frac{L_1'}{L_2}} \qquad (12)$$

If the vessel is filled with electrolyte and the quality of the coil Q is measured, then by means of equation (10) it is possible to find the numerical value of $Q_1$.

The applicability of the method of measurement chosen for the titration depends on the order of the value of Q. Thus if $Q_1 < 1$ the measuring set-up will be most sensitive to changes in $L_{int.}$. If $Q_1 > 1$, however, the most effective method of measurement will be that using a Q-meter (vide infra).

The application of the L-cell is described in a number of papers [10,17,21, 34].

Cells of the simple types have been described above. In principle it should be possible to use cells of a mixed type (LC-cells).

III

All the measuring apparatus used for registering changes in the electrolyte characteristics during H.F. titration can be divided into a number of groups according to the principles on which they are based:

1) Z-meters are used for following changes in total resistance Z; 2) Q-meters are used for measuring changes in high frequency power losses in oscillating generator circuits; 3) F-meters are used for measuring changes in frequency. 4) apparatus of a mixed type.

1) Z-meters [26,31]. If a resistance $\bar{Z}_{cell}$ is in series with the cell resistance $\bar{Z}_1$ and the e.m.f. is $\bar{U}$ then the current will be given by

$$\bar{I} = \frac{\bar{U}}{\bar{Z}_{cell} + \bar{Z}_1} . \qquad (13)$$

The current $\bar{I}$ will also change when $\bar{Z}_{cell}$ changes. Changes in I can be followed during titration. A simplified scheme of the principal parts of such an apparatus is shown in Fig. 6. A C-cell is used in this type of apparatus [15] while a galvanometer with a crystal detector is used for measuring the current.

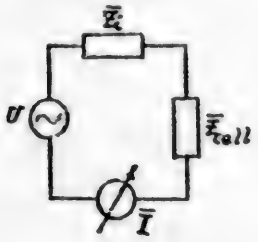



Fig. 6.

Stake [31] in his apparatus varied the sensitivity by changing $\bar{Z}_1$ (the capacity of a variable condenser through which the cell is connected to the generator is varied). It would be expedient to keep $\bar{Z}_1$ a minimum and to vary the sensitivity by changing the voltage of the generator U. In this case a given sensitivity would be achieved for a minimum value of the current through the solution. (The current density passing through the electrolyte should not exceed 50-70 $\mu A / cm^2$, otherwise there will be appreciable heating of the electrolyte).

Since frequency changes do not affect $\bar{Z}_{cell}$ and $\bar{Z}_1$ appreciably, then the requirements for frequency stabilization of the H.F. generator are not very high in this method.

2. Q-meter set-ups can basically use either the principles on which the usual Q-meters are constructed [35] or the special type of operating conditions of a self-exciting generator, where the amplitude of the oscillations generated depends strictly on the quality of the oscillating circuit. The titration process in this case is followed by observing the changes in the anode or network currents of the generator. The maximum achievable accuracy of this method is determined basically by the stability of the generator voltage.

Apparatus with generators assembled according to a set-up using a two circuit auto-generator with a common cathode have been widely used [10 16,21.32]. The amplitude of the oscillations in this case will be determined not only by the quality of the oscillating circuit in which the cell is included, but is also determined by the characteristic resonance frequency of this circuit $f_r$. This frequency $f_r$ will change during titration (see F-meters). It is better to consider apparatus with generators of this type as being of the mixed type of apparatus. The accuracy of these apparatuses is basically determined by the

stability of the voltage supply, since the amplitude of the oscillations generated in this case is strongly dependent on the operating conditions of the generator, and consequently both on anode and filament voltage respectively.

3) The apparatus most widely used is that based on the F-meter principle [11,17,19,22].

We have already noted that during titration, the cell which is connected directly to the generator circuit changes the characteristic resonance frequency of the circuit. Thus,

$$\frac{\Delta f}{f} = -\frac{1}{2}\left(\frac{\Delta C}{C} + \frac{\Delta L}{L}\right). \qquad (14)$$

where $\Delta f$ is the frequency change of the generator circuit in which the cell is included; $\underline{C}$ and $\underline{L}$ are the total capacity and inductance of the circuit including the cell; $\Delta C$ and $\Delta L$ are the changes in the equivalent capacity and inductance of the cell during titration.

During H.F. titration the value of $\Delta f/f$ is of the order of $10^{-5}$ and less, so that direct measurements of frequency changes are impossible. The heterodyne method is therefore used for measuring frequency changes during H.F. titration.

The gist of the method is as follows: the cell is included in the circuit of a self-exciting generator in such a way that the generated frequency is completely determined by the characteristic resonance frequency of the circuit $f_0$. During titration $f_1$ changes by an amount $\Delta f$, so that it is possible to write $f_1 = f_0 + \Delta f$. The frequency $f_1$ of this generator is intermixed with the frequency of an auxiliary generator $f_2$ and the differential frequency $F = f_1 - f_2$ isolated. This differential frequency is measured directly by a frequency meter. Now the relative frequency changes will be considerably greater

$$\frac{\Delta f}{F} \gg \frac{\Delta f}{f_0}, \qquad (15)$$

since $F \ll f_0$ consequently these changes can be measured more accurately. The lower $\underline{F}$, the lower the resolving power the frequency meter should have in order that it may have a given sensitivity. This differential frequency $\underline{F}$ could be chosen equal to zero, but for this purpose it would be necessary to eliminate the trapping of the frequency of one generator by the frequency of the other. Usually $\underline{F}$ is chosen to have a value of ca. $10^3$ cycles since, under these conditions the coupling-hysteresis effect is not observed even when both generators are working on fundamental frequencies.

The heterodyne method is the most sensitive method and enables titration to be carried out with accuracies of the order of a tenth and even a hundredth of a per-cent. In this case it is very important that the generator have a highly stabilized frequency, since the latter determines the accuracy of the method.

The accuracy attainable at present by using H.F. methods of titrations is not final; even the results obtained to date however show the possibilities of this method. Moreover, the use of radio apparatus for H.F. titrations opens up great possibilities for the automatization of titration.

Received February 24, 1953

## LITERATURE CITED

[1] G. G. Blake, Conductometric Analysis at Radio Frequency, London, 1950.

[2] B. J. Blaedel, H. V. Malmstadt, Anal. Chem., 22, 734 (1950).

[3] J. L. Hall, Anal. Chem., 24, 1236 (1952).

[4] K. Cruse, Z. anal. Chem., 133, 361 (1951).

[5] K. Cruse, Z. anal. Chem., 136, 129 (1952).

[6] G. V. Troitsky, Biochemistry, 5, 375 (1940).

[7] P. H. Monaghan, P. B. Moseley, T. S. Burkhalter, O. A. Nance, Anal. Chem., 24, 193 (1952).

[8] D. E. Laskowsky, R. E. Putscher, Anal. Chem., 24, 965 (1952).

[9] P. W. West, P. Senise, T. S. Burkhalter, Anal. Chem., 24, 1250 (1952).

[10] F. W. Jensen, A. L. Parrack, Ind. Eng. Chem., Anal. Ed., 18, 595 (1946).

[11] W. J. Blaedel, H. V. Malmstadt, Anal. Chem., 24, 450 (1952).

[12] R. C. Axtmann, Anal. Chem., 24, 783 (1952).

[13] Remosuke Hara, J. Pharm. Soc. Japan, 71, 1122 (1951); Chem. Abs. 46, 2436.

[14] Symposium "Use of Radiotechnical Methods in the National Economy" edited by A. I. Berg, State Energy Press, Moscow-Leningrad, p. 30.

[15] G. G. Blake, J. Sci. Instr., 22, 174 (1945); cited in Analyst 76, 241 (1951).

[16] R. Arditti, P. Heitzmann, Comptes. rend., 229, 44 (1949).

[17] P. W. West, T. S. Burkhalter, L. Broussard, Anal. Chem., 22, 469 (1950).

[18] Masaichiro Masui, Yoichi Kamura, J. Pharm. Soc., Japan, 71, 1194 (1951); Chem. Abs. 46, 2440.

[19] W. J. Blaedel, H. V. Malmstadt, Anal. Chem., 22, 1413 (1950).

[20] W. J. Blaedel, H. V. Malmstadt, Anal. Chem., 23, 471 (1951).

[21] F. W. Jenser, G. Watson, L. G. Vela, Anal. Chem., 23, 1327 (1951).

[22] W. J. Blaedel, H. V. Malmstadt, Anal. Chem., 22, 1410 (1950).

[23] O. L. Miller, Anal. Chem., 24, 1247 (1952).

[24] K. Anderson, D. Revinson, Anal. Chem., 22, 1272 (1950).

[25] W. J. Blaedel, H. V. Malmstadt, Anal. Chem., 24, 455 (1952).

[26] W. J. Blaedel, H. V. Malmstadt, D. L. Petitjean, W. K. Anderson, Anal. Chem., 24, 1240 (1952).

[27] G. Falkenhagen, "Electrolytes," Chem. Theor., 1935

[28] Symposium "Measurement of Mechanical Quantities by Electrical Methods," Machinery Press, 1952.

[29] W. J. Blaedel, T. S. Burkhalter, D. G. Flom, G. Hare, F. W. Jensen, Anal. Chem., 24, 198 (1952).

[30] G. G. Blake, Analyst 76, 241 (1951).

[31] G. G. Blake, Analyst 75, 32 (1950).

[32] J. L. Hall, Anal. Chem., 24, 1244 (1952).

[33] B. P. Aseev, "The Basis of Radiotechnics", Communications Press, 1947.

[34] K. Anderson, E. S. Bettis, D. Revinson, Anal. Chem., 22, 743 (1950).

[35] G. A. Remez, "Radiomeasurements", Communications Press, (1948).

# THE USE OF DITHIZONE AS AN EXTRACTION INDICATOR

A. G. Karabash

In addition to numerous physico-chemical methods for indicating end points in volumetric analysis, chemical indicator-reagents have been successfully developed and improved for detecting equivalence points during titration; their advantage is simplicity and rapidity of titration [1].

The intensive development of precipitation and complex formation methods is characteristic of contemporary progress in volumetric analysis, particularly in the analysis of metals, including, in this connection the use of selective organic reagents which are recommended for qualitative analysis, (particularly in spot tests) for determining the equivalence point during titration.

Numerous examples of such new, internal or external indicators [2-12] can be quoted. Nevertheless it is only possible to note solitary attempts to search for indicators used universally for various methods of volumetric analysis.

A selective indicator is a selective reagent for a particular ionic or atomic group under the titration conditions used; the selectivity of its action just as for any other chemical reagent is related to the conditions of the reaction medium.

To a large extent highly sensitive selective indicators answer the requirements of direct rapid titrations, particularly for precipitation and complex formation methods.

The use of dithizone as a selective extraction indicator is considered below.

## EXTRACTION INDICATORS AND THEIR USE

When chemical reagents are grouped according to their uses, in addition to internal and external indicators, it is rational to consider extraction indicators which are used during titration in the form of a solution in an immiscible solvent, in the layer of which all the indicator changes during titration can be followed, as an independent group.

In connection with this increasing use of organic reagents the characteristic technique of carrying out analytical operations, particularly in the form of extraction techniques, including the extraction indicator method, is also used more and more in practice.

Extraction indicators have been in use for a long time in inorganic analysis; e.g. solutions of iodine in organic solvents such as $CHCl_3$, $CCl_4$, $C_6H_6$, etc. have been used in iodometry [15-17]. Indication of the end point by iodine extraction is three times more sensitive than that of the iodine-starch reaction [18], and is applied very effectively in iodometric and iodatometric methods [18-23].

An extraction indicator method is used in neutralization methods for determination of pH, and for determining the equivalence point during titration, particularly in cases of cloudy or colored solution [24].

As examples of extraction indicator methods for reactions involving precipitation and complex formation the following may be quoted; fluorimetric determination, e.g. of aluminum with ferric thiocyanate in ether or alcohol layers as an indicator [25-27] the titration of ferric iron with ferrocyanide, using ferric thiocyanate in an isoamyl alcohol layer as indicator [28], the titration of zinc ferrocyanide and nickel cyanide using diphenylcarbazone in $CCl_4$ solution as indicator [29], the determination of picric acid and other orthopoly nitro phenols and picrates (Ca, K, nicotine, etc.) by means of methylene blue [30-32].

It should be noted that the little use made hitherto of extraction indicators in the practice of inorganic analysis does not correspond by any means to the possibilities of the method.

There is a great variety of extraction indicators. Sometimes the reacting substance is colored and is extracted in the solvent layer so that it can act as its own indicator, e.g. the solution of iodine in $C_6H_6$ or $CHCl_3$ in iodometry.

In the case of precipitation reactions and complex formation, a substance can be used as an extraction indicator, if it forms a compound (e.g. a complex) with the respective ion in solution, which can be distinguished by its color, and dissolves both in water and an immiscible organic solvent, the solubility being greater in the organic solvent. This last condition is satisfied when the distribution coefficient is favorable.

The extraction indicator is thus found predominantly in the layer of the organic solvent which is spatially separated from the sphere of action (the aqueous solution) by the surface of separation of the two liquid phases, but nevertheless through this same surface of separation the indicator is connected all the time via a mobile equilibrium with the reaction medium, and reflects all the changes which occur in the latter during titration. The first of these conditions, viz. the fact that the system consists of two phases distinguishes extraction indicators from internal indicators. The second condition, i.e. direct contact between indicator and reaction medium essentially distinguishes it from external indicators.

While possessing the characteristics of physico-chemical equilibrium conditions, extraction indicators in addition form a group which unites the essential features of the two other groups indicated above.

Extraction indicators are not so fast as internal indicators with respect to the speed with which equilibrium is attained, this speed can however be easily achieved by periodically shaking the solution during titration, thanks to the fact that the layer of organic solvent is broken up into small drops and to a significant increase in the surface of contact between the two liquid phases which results from the shaking.

The basic criteria which determine the practical value of an indicator are its selectivity (under the titration conditions) and sensitivity.

In this respect, extraction indicators have the following advantages.

1. Localization of the indicator changes in the layer (or drop) of the immiscible organic solvent eliminates interference from the reaction medium and enables one to carry out observations more readily, e.g. in the case of turbid and colored solutions, and when titrating large volumes of dilute solutions.

2. The simplicity of regulating the sensitivity of the indicator within a wide range. This is effected by changing the ratio of the volume of the two liquid phases (water and the immiscible solvent), and the concentration of the indicator and its distribution coefficient in liquids which depends both on the character of the organic solvent and on the conditions in the titration solution (pH, etc.).

3. The possibility of using as indicators, new, selective, highly sensitive organic reagents; particularly inner complex compounds, independently of the degree of their solubility in aqueous solutions.

In general the extraction technique is a very effective way of increasing the selectivity and sensitivity of analytical reactions and is widely used in colorimetric analysis for the determination of micro quantities [33].

It is natural to expect that the extraction method will find further applications for determining end points during titration.

## THE PROPERTIES OF DITHIZONE AS AN EXTRACTION INDICATOR

Dithizone (diphenylthiocarbazone) is one of the most valuable organic reagents used for the analysis of metals, and a vast amount of work has been devoted to its practical application [33-43].

Dithizone behaves like a weak acid and forms salt-like inner complex salts with a number of metals of the $H_2S$ and ammonium sulfide groups—the dithizonates are characterized by exceedingly bright colors, they are insoluble in water but dissolve readily in organic solvents.

In most of its reactions dithizone behaves as a mono-basic acid [41]. Two series of dithizones which differ in their stoichiometric ratios are known for some metals. The popular explanation of the structure of dithizone and of metallic dithizonates which postulates the existence of two tautomeric forms of the compounds—keto and enol—is not based on any experimental basis. In more recent papers it

is assumed that the acid properties of dithizone are determined by the mercapto group contained in its molecule [43].

The dithizone complexes of many metals are very stable and according to the values of their instability constants they form a series similar to the sulfides [37,41,34].

The reactions of certain metals with dithizone are selective for certain definite experimental conditions which can be achieved by regulation of the pH of the solution and the use of various complexing agents for masking. The values of the molar extinction coefficients of dithizone ($\varepsilon$ = 30,400) and of the dithizonates ($\varepsilon$ = 40,000–150,000) respectively are considerably greater than that of the majority of organic dyes [41,37]. Dithizone reactions are accordingly characterized by high sensitivity. These properties of dithizone as a reagent are widely used in practice for qualitative analysis, and particularly for the quantitative determination of traces of many heavy metals by colorimetric methods, including colorimetric titration, and volumetrically for so-called extraction titrations. In the last instance, quantitative extraction of the metallic ions is carried out by means of dithizone which acts as the titration solution [in $CCl_4$, $CHCl_3$] [38,34].

Because of the solubility of the dithizonates and of dithizone itself, and because of the stoichiometric ratios which hold during these reactions, methods involving the use of dithizone are confined to the analysis of micro-amounts of metals (usually not more than ca. 100 μg).

Lead dithizonate (in solution in $CCl_4$ or $CHCl_3$) has been used as an indicator in neutralization methods for the determination of the acidity of dark colored liquids on titration with alkali [44,24].

In the methods described below dithizone in the form of its solutions in organic solvents has been used as an extraction indicator for volumetric methods involving precipitation and complex formation when ions of the $H_2S$ group of metals participate [45]. During the titration of the metal cations with the respective precipitants or complexing agents (or during back titration) a small amount of the solution of dithizone in the organic solvent ($CCl_4$, $CHCl_3$, $C_6H_6$ toluene) which is immiscible with water is added to the aqueous solution of the salt and titration carried out with reagent solution, the latter being added in small amounts, the mixture being shaken after each addition and the color of the dithizone layer observed.

At or near the equivalence point as a result of precipitation or complex formation there is a sharp increase or decrease in concentration of the reacting metal ion with corresponding decomposition or formation of the dithizonate of the metal which is accompanied by a sudden change in color of the organic solvent.

Since free dithizone in $CCl_4$ (or $CHCl_3$ etc.) has a very intense emerald-green color, while the metal dithizonates have extremely bright and characteristic colors, under suitable titration conditions the equivalence point can be determined very accurately. This indication of the end point is based on the difference in value of the instability constants of the metal dithizonates and the instability constants or solubility products (activities) of the complex of these metals with the complexing agents or precipitants used, this difference in the values of these constants can, if required, be changed by regulating the conditions of the reaction medium (pH, addition of masking agents, etc.)

In actuality, when considering the reversible equilibrium between the two-phase system and the titration reaction, (precipitate ion or complex formation in the simplest case) [37, 41] the ratio of the two colored forms of the indicator in the organic solvent layer at the equivalence point may be expressed as follows:

$$\frac{[ND]_{or}}{[MD]_{or}} = \frac{K^{\circ}_{MD}[H^+]}{K_{ND}[M^+]_{e.p.}} = \frac{K^{\circ}_{MD}[H^+][A^-]_{e.p.}}{K^{\circ}_{ND}PR_{MA}} = \frac{K^{\circ}_{MD}[H^+]}{K^{\circ}_{ND}\sqrt{PR_{MA}}}$$

The legends used are as follows. ND – dithizone, which is represented as a monobasic acid with an anion $D^-$; $M^+$ – the cation of a univalent metal M; $A^-$ – the anion which forms a difficultly soluble (or complex) compound MA with metal M; MD – the dithizonates of the metal M; $K^{\circ}_{ND}$ and $K^{\circ}_{MD}$ – constants which take into account the total equilibrium of dithizone (ND) and dithizonate (MD), which include both the dissociation constants in aqueous solution and the corresponding distribution coefficients of the undissociated molecules between the two liquid phases [37,41]. $PR_{MA}$ – the solubility product of the compound MA.

The figures in square brackets represent the corresponding concentrations.

Thus, the choice of optimum titration conditions can be made not only empirically but also on the basis of the results of the chemical equilibrium.

A favorable ratio for the equilibrium constants indicated above under the respective medium conditions enables dithizone to be used as an extraction indicator in volumetric analysis: e.g., in argentometry, cyanometry, mercurimetry, in precipitation by sulfides and in other methods involving precipitation and complex formation, as described below.

Method Used for Titration

An aliquot of the aqueous test solution is placed in a test tube of ca. 20 ml ($\phi$ = 15 mm) or 50 ml ($\phi$ = 20 mm) capacity, fitted with a ground glass stopper, and a ca. 0.0001 M or even weaker (0.00005 M) solution of dithizone in $CCl_4$($CHCl_3$, $C_6H_6$) in amounts of ca. 1/20 – 1/10 of the volume of the aqueous solution added. Titration is carried out at room temperature (not higher than 25°) with a solution of the reagent from a buret graduated in 0.02 ml).

The reagent is added in small amounts, the solution being shaken after each addition (the test tube is stoppered) and the color of the dithizone layer observed.

Initially, the color of the indicator layer which changes on addition of the reagent, rapidly reverts to its original color on gentle shaking. Towards the end of the titration, the color changes are a bit slower and it is necessary to shake for 5-10 seconds.

The end of the titration is that point at which there is a clear-cut change in the dithizone color in the $CCl_4$ layer which does not disappear on further shaking of the liquid for ca. 30 seconds, and which is characteristic of the formation or decomposition of the respective dithizonates of the reacting metal. In order to be certain that the end point has been reached, an excess of 1-2 drops of reagent is added which is not taken into account.

One titration takes about 5-7 minutes.

The reagent solution is standardized with the respective standard solution under identical conditions (concentration, volume and composition of the solution) or the reagent solution is made up using a known weight of reagent.

The following notes may also be necessary.

1. During titration it is essential that the optimum conditions for the given method must be maintained, particularly the pH of the solution. Addition of alkali or acid must be carried out accurately.

2. The indicator solution of dithizone in $CCl_4$ (or $CHCl_3$ $C_6H_6$) is prepared in the usual way, observing all the conditions when working with dithizone (screening it from heat and light in a dark covered bottle.)

The dithizone preparation may be given a preliminary purification if necessary by successive extractions from ammoniacal and sulfuric acid solution.

3. The molarity of the dithizone solution can be checked if necessary by an extraction titration with standard silver solution.

It is recommended that the sensitivity of the indicator solution be checked under identical conditions to those used for titration, i.e., the indicator error which is usually negligible, is determined, although it must only be taken into account when doing micro-determinations.

4. The sensitivity of the dithizone indicator solution for the various cases (macro, micro, and semi-micro) during titration can be regulated by varying the amount used and its concentration in the organic solvent.

For the titration of dilute solutions and also for micro-determinations, the minimum amount of dithizone indicator solution is used (as weak as possible, e.g., 0.00005 M), while the reagent used for the titration should not be too weak.

5. Oxidizing agents such as $Fe^{3+}$, oxides of nitrogen, and others, must be absent in the titration solution. $HNO_3$ can be allowed. If other metals are present (i.e., different from those being determined), then the extraction of their dithizonates in the indicator layer must be taken into account.

TABLE 1

Titration of Silver with a Solution of Iodide, and the Argentometric Determination of Iodide using Dithizone as an Extraction Indicator

| Number | Used for titration | | | | 0.025 M KI used in ml | Concentration of acid in equivalents N $H_2SO_4$ |
|---|---|---|---|---|---|---|
| | $H_2SO_4$ dilute (1:3), in ml | water in ml | $8 \cdot 10^{-5}$ solution of dithizone in $CCl_4$, in ml | 0.025 M $AgNO_3$, in ml | | |
| 1 | 0.5 | 3.5 | 0.5 | 1.00 | 1.02 | 0.8 |
| 3 | 3.0 | 1.0 | 0.5 | 1.00 | 1.00 | 4.6 |
| 6 | 1.0 | 4.0 | 1.0* | 2.00 | 2.00 | 1.0 |
| 7 | 2.5 | 2.5 | 1.0 | 2.00 | 2.00 | 2.6 |
| 11 | 5.0 | – | 1.0 | 5.00 | 5.00 | 3.1 |
| 14 | 15.0 | – | 2.0 | 10.00 | 10.01 | 4.0 |
| | 0.1N $HNO_3$ | | solution of 0.5 % eosin | | | Fajans titration |
| 17 | 0.5 | 3 | 0.1 | 2.00 | 2.00 | |
| 19 | 0.5 | 3 | 0.1 | 5.00 | 5.00 | |
| | $H_2SO_4$ dilute (1:3) in ml | | $8 \cdot 10^{-5}$ M solution of dithizone in $CCl_4$, in ml | 0.025 M KI in ml | 0.025M $AgNO_3$, in ml | |
| 21 | 2.5 | 2.5 | 1.0 | 2.00 | 2.00 | 2.6 |
| 23 | 3.0 | 1.0 | 1.0 | 3.00 | 3.00 | 2.8 |
| | $H_2SO_4$ dilute (1:3) in ml | | $5 \cdot 10^{-5}$ M solution of dithizone in $CCl_4$, in ml | 0.0025 M $AgNO_3$, in ml | 0.0025 M KI, in ml | |
| 26 | 1.0 | 1.0 | 0.4 | 0.50 | 0.50 | 3.1 |
| 27 | 1.0 | 1.0 | 0.4 | 1.00 | 1.00 | 2.3 |
| 29 | 1.0 | 0.5 | 0.4 | 2.00 | 2.01 | 1.7 |
| 30 | 2.0 | 1.0 | 0.4 | 3.00 | 3.00 | 2.0 |

## Description of the Methods Used

### 1. Determination of the Silver Ion $Ag^+$

a) By titration with the $I^-$ ion. Titration of 0.01 N or more dilute solutions (down to 0.001 N) with KI is carried out in $H_2SO_4$ solution within the limits 1.0-9.0 N $H_2SO_4$ (acid dilution by volume 1:30-1:3), the optimum acidity being 3-4 N $H_2SO_4$. The indicator solution used is a $1 \cdot 10^{-4}$-$5 \cdot 10^{-5}$ M solution of dithizone in $CCl_4$ (or in $C_6H_6$, toluene, etc.)

The change in indicator color at the equivalence point is very sharp (0.01 ml of a solution of 0.002 M KI is enough to produce a change), from a canary-yellow to an emerald-green.

The results obtained by this method are in exact agreement with titrations of $Ag^+$ with KI using Fajans method with eosin as an adsorption indicator, but the end point given by dithizone is considerably more sensitive than that of eosin. The results, both micro and semi-micro, are given in Table 1.

* In experiment No. 6 the indicator was a solution of dithizone in benzene.

TABLE 2

The Titration of Silver with Solutions of Bromides and Thiocyanates, and the Argentometric Determination of Bromides and Thiocyanates using Dithizone as an Extraction Indicator

| Number | Used for Titration | | | | Amount of solution used, in ml | Concentration of acid N, $H_2SO_4$, in equivalents |
|---|---|---|---|---|---|---|
| | $H_2SO_4$ dilute (1:3) in ml | Water (ml) | $1\cdot10^{-4}$ M solution of dithizone in $CCl_4$ in ml | 0.025 M $AgNO_3$ in ml | | |
| | | | | | 0.025 M KBr | |
| 2 | 2.0 | 2.0 | 0.5 | 1.00 | 1.00 | 3.1 |
| 4 | 5.0 | – | 1.0 | 2.00 | 2.00 | 5.1 |
| 6 | 5.0 | – | 1.0 | 3.00 | 3.01 | 4.2 |
| | | | | | 0.025 M KCNS | |
| 8 | 2.5 | 1.0 | 0.5 | 1.00 | 1.01 | 4.2 |
| 9 | 3.0 | 1.0 | 0.5 | 1.00 | 1.00 | 4.6 |
| 11 | 5.0 | 1.25 | 1.0* | 2.00 | 2.00 | 4.5 |
| 16 | 15.0 | – | 2.0 | 10.00 | 10.01 | 3.9 |

b) By titration with $Br^-$. Titration with 0.01 N KBr is carried out in $H_2SO_4$ solution at an acidity of not less than 2N $H_2SO_4$; the optimum is ca. 4N $H_2SO_4$ (dilution 1:9 by volume).

The end point is determined with dithizone as described above. The results are given in Table 2.

c) By titration with $CNS^-$. Titration with 0.01 N KCNS is carried out in not less than 3.5 N $H_2SO_4$; optimum 5-6 N $H_2SO_4$ (i.e., at a dilution of 1:6 by volume).

The end point is determined with dithizone, as described above. The results are given in Table 2.

2. Determinations of $I^-$, $Br^-$, and $CNS^-$ by Titration with $Ag^+$

These determinations are carried out under the conditions described above.

3. Determination of $Cl^-$.

This can be done indirectly by a back titration of excess $AgNO_3$ with KI after filtering off the AgCl precipitate.

4. Determination of $CN^-$.

Two variants of the argentometric method for cyanides were investigated.

a) Titration of the cyanide in a weakly alkaline solution (0.3-0.6 N $NH_4OH$ or 0.1-0.2 N NaOH) with $AgNO_3$, using a 0.01% solution of dithizone in $CCl_4$ as indicator.

At the end point the aqueous solution, which has up to this point a weak yellow color, acquires a reddish-rose color, while on slight shaking the yellowish layer of the $CCl_4$ solution changes to a violet-red color.

The change in color of the indicator layer during extraction titration is very sharp – 0.02 ml of 0.025 N $AgNO_3$ being sufficient to effect the change. When a small excess of $AgNO_3$ is added a bulky, flocculent, violet-red precipitate of silver dithizonate floats on the surface of the $CCl_4$ layer.

Silver can be titrated in this way with a solution of cyanide. When this is done the silver dithizonate, which is only very slightly soluble in $CCl_4$, transfers its weak yellow color to the $CCl_4$ layer; in this case an indication of the end point is given by the flotation of the violet-red precipitate of dithizonate in equilibrium in the $CCl_4$ layer or on the surface separating the $CCl_4$ and water layers. On the other hand, silver dithizonate dissolves readily in chloroform, imparting to it an intense yellow color. Therefore, if a ca. 0.01% solution of dithizone in $CHCl_3$ is used as an indicator in the cyanide titration outlined above, the weak yellowish color of the $CHCl_3$ layer changes sharply to a canary-yellow at the end point.

* In experiment No. 11 the dithizone was dissolved in toluene.

TABLE 3

The Argentometric Titration of Cyanides Using Dithizone as an Extraction Indicator

| Number | Taken for titration: $NH_4OH$ 10% in ml | Water, in ml | $1 \cdot 10^{-3}$ M solution of dithizone in $CCl_4$, in ml | ~0.05 M KCN, in ml | Ml of 0.025 M $AgNO_3$ used | Notes |
|---|---|---|---|---|---|---|
| 1 | 0.5 | 4.0 | 1.0 | 1.00 | 1.02 | |
| 3 | 0.7 | 3.0 | 1.0 | 2.00 | 2.04 | In experiments 1-10 the indicator was dithizone in $CCl_4$ |
| 6 | 1.0 2N NaOH | — | 1.5 | 5.00 | 5.05 | |
| 8 | 0.3 | 3.0 | 1.0 | 2.00 | 2.05 | |
| 10 | 0.5 | 1.0 | 1.5 | 5.00 | 5.03 | |
| | $NH_4OH$, 10% in ml | | 0.3 M KI, in ml | | | |
| 12 | 0.5 | 3.0 | 0.2 | 2.00 | 2.04 | Denizh titration |
| 15 | 0.5 | — | 0.2 | 5.00 | 5.03 | |
| | $NH_4OH$, 10% in ml | | $1 \cdot 10^{-3}$ M solution of dithizone in $CHCl_3$, ml | 0.050 M KCN in ml | | In experiments 16-26 the indicator was lead dithizonate in $CHCl_3$; 0.05 ml of 0.025 M $Pb(NO_3)_2$ was preliminarily added to all the solutions. |
| 16 | 0.3 | 5.0 | 1.0 | 1.00 | 1.00 | |
| 20 | 0.5 | 4.0 | 1.0 | 2.00 | 1.99 | |
| 21 | 0.5 | 3.0 | 1.5 | 3.00 | 2.98 | |
| 23 | 0.8 | 1.0 | 2.0 | 5.00 | 4.95 | |
| 24 | 0.8 | 1.0 | 2.0 | 5.00 | 4.96 | |
| 26 | 1.0 | 1.0 | 3.0 | 10.00 | 9.93 | |
| | | | 0.2 M KI, in ml | | | |
| 27 | 0.5 | 3.0 | 0.2 | 3.00 | 2.98 | Denizh titration |
| 29 | 0.5 | 3.0 | 0.2 | 2.00 | 1.99 | |

b. By the use of a solution of lead dithizonate in chloroform as an extraction indicator.

The titration is carried out under the same conditions as for the first variant. To a weak alkaline solution (0.3-0.6 N $NH_4OH$) of cyanide is added one drop of 0.025 M $Pb(NO_3)_2$ and then 1-2 ml of 0.01% dithizone in $CHCl_3$. After shaking, the $CHCl_3$ layer acquires a carmine-red color because of the lead dithizonate dissolved in it.

During titration, the white precipitate of silver cyanide which forms on addition of $AgNO_3$ dissolves on mixing. The end point, which is a sharp change in the $CHCl_3$ layer from carmine-red to a canary-yellow, is determined by the formation of silver dithizonate on the appearance of a very small excess of $Ag^+$ ions in the solution (from 0.01-0.02 ml of 0.025 N $AgNO_3$).

Because of large differences in the instability constants of lead and silver dithizonate, respectively, a clear-cut selective extraction of the silver dithizonate with the $CHCl_3$ occurs. A back titration can be done in the same way. Both variants (a) and (b) gave identical results.

During the argentometric determination of cyanides by the second variant (b) it was established that the presence of a small amount of Zn in the test solution (in molar ratios $ZnSO_4$ : KCN = 1:5) does not affect the results.

The presence of $[K_4Fe(CN)_6]$ in solution under the conditions described above does not interfere with the determination of $CN^-$ either.

TABLE 4

Titration of Mercuric Salts with Iodide Using Dithizone as an Extraction Indicator

| Number | Concentrated $H_2SO_4$ (in ml) | Taken for titration Water (in ml) | $1 \cdot 10^{-4}$ M solution of dithizone in $CCl_4$, (in ml) | Standard solution of ca. 0.0125 M $HgSO_4$ (in ml) | Ml of 0.025 KI used | Concentration of acid N·$N_2SO_4$ |
|---|---|---|---|---|---|---|
| 1 | 1.0 | 2.0 | 1.0 | 1.00 | 0.98 | 7.4 |
| 7 | 1.0 | 4.0 | 1.5* | 1.00 | 0.98 | 5.3 |
| 3 | 1.25 | 3.75 | 1.5 | 2.00 | 1.95 | 5.1 |
| 6 | 2.5 | 2.5 | 2.0 | 2.00 | 1.96 | 10.2 |
| | $H_2SO_4$ dilute (1:3), in ml | | | | 0.025 M KI, in ml | |
| 8 | 2.5 | – | 0.5 | 0.10 | 0.97 | 6.5 |
| 10 | 2.5 | – | 0.5 | 0.10 | 0.96 | 6.5 |
| 11 | 2.0 | – | 0.5 | 0.050 | 0.48 | 7.3 |
| 12 | 2.5 | – | 0.5 | 0.050 | 0.49 | 7.5 |

In parallel with the methods described above, the test solution of cyanides was also titrated with $AgNO_3$ using the Liebig-Denizh method with KI as an indicator (turbidimetric). Indicator correction in this case amounted to 0.02 ml of 0.025 N $AgNO_3$.

The results obtained are in good agreement with previous ones (vide Table 3). As compared with the Liebig-Denizh method, however, the argentometric determination of cyanide by means of dithizone as the extraction indicator has the advantage of being more convenient, and also enables the end point to be determined more accurately, particularly in the second variant, when lead dithizonate is used.

5. The Determination of $Hg^{2+}$ by Titration with $I^-$

The titration of 0.02-0.002 M solutions of mercuric salts with KI is carried out in $H_2SO_4$ solution at a dilution of $H_2SO_4$: $H_2O$ (by volume) of not less than 1:4, the optimum being ca. 1:3 (but not more than 1:2).

The change in color of the dithizone layer (in $CCl_4$ or $C_6H_6$) from orange-yellow to dark red is very sharp, 0.01-0.02 ml of 0.002 M KI being sufficient to effect the change (vide Table 4).

The end point corresponds to the equation:

$$Hg^{2+} + 2I^- \longrightarrow HgI_2$$

6. The Determination of Gold $Au^{3+}$ by Titration with Thiosulfate

The titration of auric chloride in 0.5-1.0 M solution of HCl saturated with chloride (KCl, NaCl) is carried out with a 0.01-0.002 N solution of $Na_2S_2O_3$ using a ca. 0.01% solution of dithizone in $CCl_4$ (Table 5).

In the saturated solution of chloride (KCl, NaCl) the layer of gold dithizonate in the $CCl_4$ is intensely colored a gold-yellow, which changes into an emerald-green on addition of a small excess of $Na_2S_2O_3$.

7. Determination of Heavy Metals by Titration with Sulfide ($Na_2S$)

a) Titration of $Pb^{2+}$ and of $Cd^{2+}$ is effected with a solution of 0.01-0.005 M $Na_2S$ in neutral solution in the presence of boric acid ($H_3BO_3$).

The change of color of indicator – a solution of dithizone in benzene – is very sharp, from a light red to an emerald green.

* In Experiment 7 the indicator used was dithizone in benzene.

TABLE 5

Titration of Gold with Thiosulfate Using Dithizone as an Extraction Indicator

| Number | Taken for Titration | | | | | Ml of 0.009575 N $Na_2S_2O_3$, in ml |
|---|---|---|---|---|---|---|
| | solution of 10% HCl, in ml | water, in ml | KCl crystallization | $1 \cdot 10^{-4}$ M solution of dithizone in $CCl_4$ in ml | $Au^{3+}$ µg | |
| 1 | 1.0 | 3.0 | to saturation | 1.0 | 500 | 0.57 |
| 3 | 1.0 | 2.0 | " | 1.0 | 1000 | 1.16 |
| 6 | 1.0 | 1.0 | " | 1.0 | 1500 | 1.75 |
| | | | | | | 0.002 N $Na_2S_2O_3$, in ml. |
| 8 | 1.0 | 1.0 | " | 0.3 | 100 | 0.55 |
| 11 | 1.0 | 1.0 | " | 0.3 | 250 | 1.36 |
| 13 | 2.0 | 1.0 | " | 0.3 | 500 | 2.73 |

TABLE 6

Titration of Hg, Ag, Pb, Bi, Cd with $Na_2S$ and the Determination of Sulfide Sulfur ($S_2$) by Titration with the Salts of These Metals Using Dithizone as an Extraction Indicator

| Number | Taken for Titration | | | | Reagent solution used in ml |
|---|---|---|---|---|---|
| | $H_2SO_4$ concentration in ml | water in ml | $1 \cdot 10^{-4}$ M solution of dithizone in $CCl_4$ in ml | Test solution in ml | |
| | | | | 0.0125M $HgSO_4$ | $Na_2S$ solution |
| 3 | 0.7 | 2.3 | 2 | 2.00 | 2.79 |
| 4 | 0.5 | 2.5 | 2 | 2.00 | 2.80 |
| | | | | $Na_2S$ solution | 0.0125 M $HgSO_4$ |
| 7 | 0.3 | 1.7 | 2 | 3.00 | 2.05 |
| 8 | 0.3 | 1.7 | 2 | 3.00 | 2.06 |
| | | | | 0.025 M $AgNO_3$ | $Na_2S$ solution |
| 10 | 0.3 | 4.2 | 2 | 0.50 | 0.73 |
| 12 | 0.8 | 3.2 | 2 | 1.00 | 1.48 |
| | | | | $Na_2S$ solution | 0.025M $AgNO_3$ |
| 13 | 0.3 | 2.7 | 2 | 2.00 | 1.30 |
| 14 | 0.3 | 2.7 | 2 | 2.00 | 1.32 |
| | $H_2SO_4$ (1:3) | | | $Na_2S$ solution | 0.0025M $HgSO_4$ |
| 15 | 0.2 | – | 0.5 | 1.00 | 0.74 |
| 16 | 0.2 | – | 0.3 | 1.00 | 0.74 |
| 17 | 0.2 | – | 0.5 | 2.00 | 1.48 |
| | $H_3BO_3$ in g | | | 0.025 M $Pb(NO_3)_2$ | $Na_2S$ solution |
| 19 | 0.5 | 2.0 | 0.5 | 0.10 | 0.40 |
| 23 | 1.0 | 3.0 | 1.5 | 0.30 | 1.20 |
| | $H_3BO_3$ in g | | | 0.025 $CdCl_2$ in ml | $Na_2S$ solution |
| 25 | 0.5 | 1.0 | 0.5 | 0.10 | 0.40 |
| 28 | 1.0 | 1.5 | 1.0 | 0.20 | 0.80 |
| 30 | 1.0 | 1.5 | 1.0 | 0.30 | 1.20 |
| | $NaHCO_3$ in g | | | 0.01 M $Bi(NO_3)_3$ | $Na_2S$ solution |
| 31 | 0.5 | 2.0 | 1.5 | 0.20 | 0.52 |
| 32 | 0.5 | 2.0 | 1.0 | 0.20 | 0.52 |
| 33 | 0.5 | 2.0 | 1.5 $CCl_4$ | 0.40 | 1.04 |

b) $Bi^{3+}$ is titrated with 0.005 M $Na_2S$ in the presence of sodium bicarbonate. The change in color of the dithizone in benzene or $CCl_4$ indicator is very sharp from orange-yellow to emerald-green.

c) $Hg^{2+}$ and $Ag^+$ are titrated with a 0.01 M solution of $Na_2S$ in a weak $H_2SO_4$ medium.

The change in color of the dithizone in benzene indicator is very sharp from an orange ($Hg^{2+}$) or canary yellow ($Ag^+$) to emerald green.

8. Determination of Sulfide Sulfur ($S^{2-}$ Ions) by Titration with Solutions of Heavy Metal Salts was carried out under similar conditions using a solution of dithizone in benzene or $CCl_4$ as indicator.

Results for the determinations of the metals' ions and of sulfide sulfur are given in Table 6.

The results given in Tables 1-6 are typical of the large number of experiments (1500 volumetric determinations were made altogether). The results obtained using dithizone as an extraction indicator are characterized by their reproducibility and high accuracy.

## SUMMARY


1. The characteristics of extraction indicator methods are considered.

2. Dithizone (diphenylthiocarbazone) has been used as an extraction indicator for volumetric analysis in methods involving precipitation and complex formation in which metals of the $H_2S$ group participate.

The method is based on the formation or decomposition of metallic dithizonates at the titration end point, which is accompanied by a sharp change in the color of the organic solvent layer ($CCl_4$, $CHCl_3$, $C_6H_6$).

3. The series of experiments carried out show the expediency of using dithizone as an extraction indicator in the following methods for the determination of ions:

argentometry – $Ag^+$ ($I^-$, $Br^-$, $CNS^-$),
cyanometry – $Ag^+$, $CN^-$
mercurimetry – $Hg^{2+}$, $I^-$
precipitation with sulfides – $Hg^{2+}$, $Ag^+$, $Pb^{2+}$, $Bi^{3+}$, $Cd^{2+}$, $S^{2-}$;
determination of $Au^{3+}$ with $S_2O_3^{2-}$.

The optimum conditions for the medium (pH of the solution) favorable to the accurate titration of each of the ions indicated above have been worked out.

In these methods, from the point of view of selectivity, high sensitivity, and accuracy of results, dithizone excels the usual external indicators recommended in classical methods.

4. The respective macro-, micro- and semi-micro methods were used.

For the latter, the use of dithizone as extraction indicator is of particular interest.


## LITERATURE CITED


[1] I. V. Tananaev, Yu. Yu. Lurye, Factory Labs, 7, 525 (1939).

[2] V. I. Kuznetsov, Proc. All-Union Conference on Anal. Chem. 1, 86 (1939).

[3] A. S. Vetrov, Proc. Commiss. Anal. Chem., III (VI) 302, (1951).

[4] I. M. Dubnikov, I. F. Tikhomirov, Factory Labs. 7, 773 (1947).

[5] M. I. Levina, I. V. Tananaev, Factory Labs, 13, No.3, 378 (1947).

[6] I. G. Urusovskaya, P. I. Zhilina, Factory Labs 15, No. 6, 749, (1949).

[7] I. M. Kolthoff, V. A. Stenger, "Volumetric Analysis" II (1952) 308,309,340,347 348,366, 378,380-392, 397-418, 254,378.

[8] G. Lendel, D. Hoffman, G. Bright, "Analysis of Ferrous Metals" 284 (1934).

[9] I. V. Dubsky, J. Trtilek, Mikrochemie, 12 (1932-1933); Mikrochemie, 15, 95-98 (1934).

[10] Hidehiro Goto, Seiichi Sato, Chem. Abs., 41, 10, 3010 (1947).

[11] E. Percs, Ber. Ungar. Pharm. Gesellschaft, 449 (1939).

[12] W. Kirsten, I. Alperowicz, Mikrochemie, 39, 3, 234 (1952).

[13] E. Schulek, P. Rozsa, Z. anal. Chem. 115, 185-195 (1939).

[14] G. A. Pevtsov, J. Anal. Chem. 4, 6, 332 (1949).

[15] "Analytical Chemistry," edited by D. I. Mendeleev, SPB(1866).

[16] B. Shevtsov, Z. anal. Chem., 44, 86-88 (1905).

[17] B. M. Margosches, Z. anal. Chem. 44, 392-395 (1905).

[18] I. M. Korenman, "Quant. Microchem. Analysis" (1949) also "Quant. Microchem. Analysis" (1936) 111, 130, 140-142.

[19] I. M. Kolthoff, "Volumetric Analysis" Part II, 65, 352, 353, 449-451 (1932).

[20] V. Gillebrand, G. Lendel, "A Practical Handbook on Inorganic Analysis", 370 (1937).

[21] S. Yu. Feinberg, "Technical Analysis of Non-Ferrous Ores," 60, (1946).

[22] E. W. Hammock, K. A. Brown, E. H. Swift, Anal. Chemistry," 20, 11, 1048 (1948).

[23] "The Analysis of Aluminum and Its Alloys", 25-27, (1947).

[24] Yu. V. Karyakin, "Acid-Base Indicators" 169, 172 (1951).

[25] A. Greef, Ber. 46, 2511 (1913).

[26] I. V. Tananaev, M. I. Levina, Factory Labs, 11, 804 (1945).

[27] I. V. Tananaev, Proc. Commiss. Anal. Chem. 1 (IV), 24 (1947).

[28] M. A. Bodin, Factory Labs. 8, 1, 32 (1939).

[29] B. S. Evans, The Analyst, 71, 847, 455-459 (1946).

[30] A. Bolliger, Sydney University reprints, 3, 14-25 (1936).

[31] I. M. Korenman, "Quant. Microchem. Anal." 228 (1949).

[32] N. S. Drozdov, N. P. Materanskaya, J. Anal. Chem. 2, 17, (1947).

[33] E. Sendel, "Colorimetric Determination of Traces of Elements", (1949).

[34] F. Welcher, Organic Analytical Reagents, III, 463-550 (1949).

[35] L. M. Kulberg, "Synthesis of Organic Reagents", 71-74 (1947).

[36] N. I. Blok, "Qual. Chem. Anal." 166, (1952).

[37] A. K. Babko, A. T. Pilipenko, "Colorimetric Anal." 30, 320-341 (1951).

[38] H. Fischer, Z. ang. Chem., 42, 43, 1025 (1929); 47, No. 40, 685-692 (1934).

[39] F. T. Beaumont, Metallurgia, 29, 172, 217-220 (1944).

[40] I. M. Kolthoff, E. B. Sandell, J. Am. Chem. Soc., 63, 1906-1908 (1941).

[41] A. K. Babko, A. T. Pilipenko, J. Anal. Chem., 1, 5-6, 275 (1946), 2, 1, 33-42 (1947).

[42] L. M. Kulberg, "Organic Reagents in Anal. Chem." 36, (1950).

[43] H. Irving, C. F. Bell, Nature 169, 4305, 756 (1952); J. Chem. Soc., 4, 1216 (1952).

[44] W. Hirsch, The Analyst, 73, 864, 160 (1948).

[45] A. G. Karabash, Author'sThesis, 76218, May 28, 1949.

February 12, 1953

# THERMAL ANALYSIS WITH REGISTRATION OF THE VOLUME OF GAS EVOLVED

B. Ya. Teitelbaum and L. G. Berg

The A. E. Arbuzov Chemical Institute of the Kazan Branch of the USSR Academy of Sciences

Thermal analysis involving registration of the heating curves on a Kurnakov [1] pyrometer, and the use of simple and differential temperature recorders (thermograph) has been widely used [2]. This method of analysis gives the phase characteristics of the component parts of a complex mixture, as a result of which it has proved essential for investigations of various metals and alloys, minerals, rocks and ores. Recently it has become possible to apply the thermograph for quantitative phase analysis as well, by measuring the reading of the differential recorder with a planimeter. [3]

Many of the thermal effects revealed by the thermograms are related to gas evolution processes. Measurement of the volume of the gases evolved can be a new and effective method for quantitative phase analysis [4] which is more accurate than the thermographic method, and should find wide application. The most expedient means of realizing this method is the automatic registration of the volume of gas at the same time as the temperature curves are recorded on a Kurnakov pyrometer.

The requirements for registering gas evolution processes led us to construct an apparatus [5] which works on the principle of measuring the resistance of a platinum (or nichrome) wire stretched along the axis of a gas buret filled with mercury. The amount of mercury which flows into the communicating vessel depends on the volume of gas entering the buret, so that the acting length of the wire increases. The resistance of the wire is measured with a resistance bridge balanced at its middle. A mirror galvanometer giving direct readings on photographic paper fixed to the drum of a Kurnakov pyrometer serves as the indicator.

The drawback of the apparatus which has been described before was that the mercury flowing from the buret created a gas pressure in the buret which differed from atmospheric pressure, and varied during the experiment; this necessitated introducing corrections or carrying out special graduations for each reaction vessel, and led to considerable irregularity in the volume scale on the photogram obtained. Moreover, in a number of cases a change in pressure from normal is not admissible.

The self-compensating buret which is of a new design (see plate, page 213) is free from these draw-backs. Automatic compensation of the mercury in buret A and in the communicating vessel (B) is realized by moving B up or down by means of motor (E) which can rotate either way. The motor is controlled through a system of relays when contact is established via the auxiliary mercury manometer (C) connected to the buret. When the pressure in the buret (and in the manometer) increases or decreases as a result of gas coming in or going out respectively the compensating vessel containing the mercury is lowered or elevated until normal pressure is again established in the buret.

The apparatus is mounted on a wooden board (180 x 900 mm) and is fixed vertically on four nails embedded on the main side. On the outside surface the following items are fixed: a 100-ml glass buret, a manometer, a three-way tap and the compensating vessel containing mercury, suspended on a cat-gut from the motor pulley. Clamps are also fitted on this die for switches (F) and indicators. All the electrical set-up is mounted on the back surface of the board which is 12 cm from the wall.

Three contacts are introduced into the U-shaped manometer: the middle and right hand side contacts are fused directly into the glass. The other side contact is regulated; it is fused into the glass tube inserted into the left limb of the manometer. The amount of mercury poured into the manometer is such that there is only a small gap between its surface and the side contacts. The smallest change in pressure in the buret leads to a rise of mercury in one of the manometer limbs to the contact, as a result of which the cathode circuit of the electronic relay is closed.

The twin relay is mounted on the base of a radio transformer FLS-2 with a converted setting. The relay consists of two parts working independently of each other, one comes into action when the left hand container of the manometer is closed, while the other operates when the right hand contacts of the manometer are closed. The anode current which thereupon comes into action operates the corresponding electromagnetic relay of a telephone type which switches on the current in one of the wires of the electric motor (for clockwise or anti-clockwise rotation). The electronic relays work on 6P3 of 6P6 tubes. An electrolytic condenser is included in parallel to avoid jarring the telephone relay.

In this set-up a universal 12 V electric motor with reducing gear was used (clockwise or anti-clockwise rotation). In order to supply the motor a winding was added to the transformer to give 12 V, and to ensure a current of 2 A*. In addition to the relay the motor can be brought into action by means of press buttons, one of which ensures a clockwise rotation and the other the reverse.

Release switches are fitted below the motor pulley, through the forks a thread passes, on which the leveling vessel is suspended. During the upward motion to the extreme position a knot on the thread pushes the form of one of the release switches and shuts off the current even when the relay or press buttons are still switched on. This prevents accidents which can occur if the vessel containing the mercury tightens on the rotating pulley. The other release switch (not shown in the diagram) acts when the buret is at its lowest point.

G, H and I on Figure 1 represent the drum, motor and pyrometer illuminator respectively.

The resistance bridge is assembled on a small ordinary strip of thin Getinax. The resistances are wound from manganin or constantan wire. All the contacts are soldered with tin.** The bridge is fed from a 4-6 V accumulator or with a rectified grid current. If the latter is used a stabilizer must be used since voltage variation distorts the photograms. The stabilized main voltage is stepped down to 4-6 volts as indicated on the diagram by means of a separate transformer and is rectified by means of a selenium rectifier. An accumulator, however, gives better results. An additional resistance can be included in series with the mirror galvanometer according to its sensitivity. Accurate regulation which enables the volume to be registered on the photographic paper is realized by using a variable resistance $R_6$.

Thermal analysis involving registration of the volume of gas evolved requires some special apparatus. Heating the test material in the usual open crucibles is impossible in this case. Though only a small amount of material is used (0.1-0.2g) the clearness of the thermographic registration is not less than when normal amounts (2-5 g) are used; in fact the accuracy increases significantly, since the time which each process takes decreases and the heat inertia also decreases. Thus, on the records of processes in which large amount of material are used, e.g., the dissociation of dolomite ($t = 760°$) is partially superimposed on the decomposition process of calcite ($t = 900°$), while when small amounts are used these two effects are clearly distinguishable because of the rapidity of heating (Figures 2 and 3).

The sample (just like a standard for the differential thermo-couple) is placed in a quartz (or, for temperatures below 600°, heat-resistant glass) 30 x 5 mm micro-tube. The micro-tube 1 with the sample is placed in the reaction vessel 2 shown in Figure 4. A thermo-couple in a porcelain tube 8 is introduced into the same place. A glass nozzle, 6, smeared with grease is fitted on the end of the thermo-couple tube to ensure that the lead from the thermocouples is hermetically sealed, while a rubber collar hermetically joinds the thermo-couple tube with the reaction vessel. The latter is made of quartz or heat-resistant glass. The micro-tube plus standard and differential thermocouples are placed in a long narrow tube made from the same material as the reaction vessel; this need not necessarily be hermetically sealed. The widened part 3 of the tube is the point at which calcium hydride is placed when the gaseous product is water. Water vapor reacts with the hydride to yield a stoichiometric amount of hydrogen, which is then measured. A tube 4 which is fused into the widened part of the apparatus serves as outlet. The reaction vessel is introduced into one of the channels in a block of stainless steel up to the point indicated on the diagram by the dotted line. (The tube containing the standard is placed in the other block channel to the same point). The block is in the form of a cylinder 24 x 150 mm with two channels parallel to the axis. The block, which is wrapped in asbestos paper, is then placed in a horizontal tubu-

*Connecting the windings of the tube filaments in order to get 11-12 V is inadmissible, because when this is done the two parts of the set-up are connected.

**Resistances $R_3$ and $R_4$ = 10 Ω. $R_2$ = 300Ω. $R_5 = R_1/2 = 300Ω$, where $R_1$ is the resistance of the platinum or nichrome wire (cross-section 0.1-0.2 mm) fused into buret A. The value of the variable resistance $R_5$ chosen depends on the sensitivity of the galvanometer K.

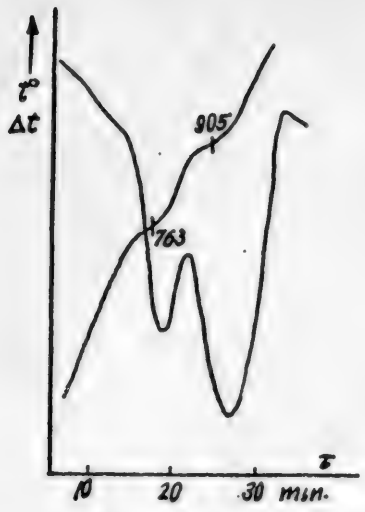



Figure 2 Thermogram for dolomite (wt 3 g)

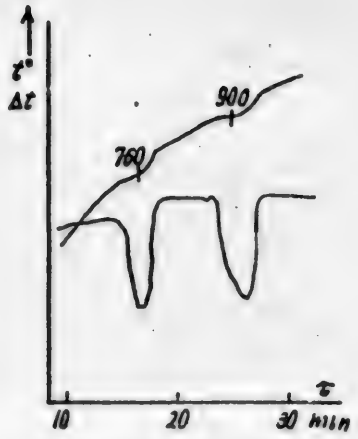



Figure 3. Thermogram for dolomite (wt 0 15 g)

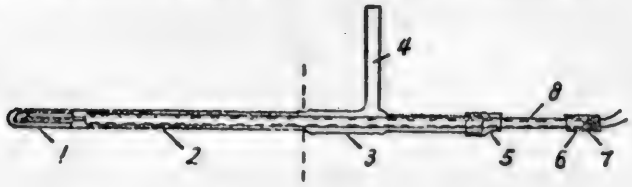



Figure 4. The reaction vessel and the method used for sealing it (schematic)

lar oven which can be controlled to give even heating (the best is a linear rate of heating). It is important that both the channels in the block are in a horizontal plane so as to ensure equal heating conditions for sample and standard

When the test material melts during the heating the oven must be inclined so that the melt cannot flow out of the tube.

The method described above was designed for investigating processes occurring during the thermal decomposition of various substances. We shall give an example of the thermograms obtained – a record obtained for the dehydration of the septihydrate of magnesium sulfate.* Only 0.0989 g of $MgSO_4 \cdot 7H_2O$ was used. Examination of the photograms on Figure 5 clearly shows that the thermal processes which occur at temperatures below 100° are not connected with the evolution of water vapor but correspond to an incongruent melting of the hydrates. The step-like shape of the curve recorded for the volume of gas liberated indicates a step-like character for the dehydration process. It is thus possible to make quantitative calculations and to determine the composition of the intermediate hydrates. The considerable stability of the unihydrate $MgSO_4 \cdot H_2O$ (kieserite) as compared with the other intermediate forms is another noteworthy fact: it is stable within the range

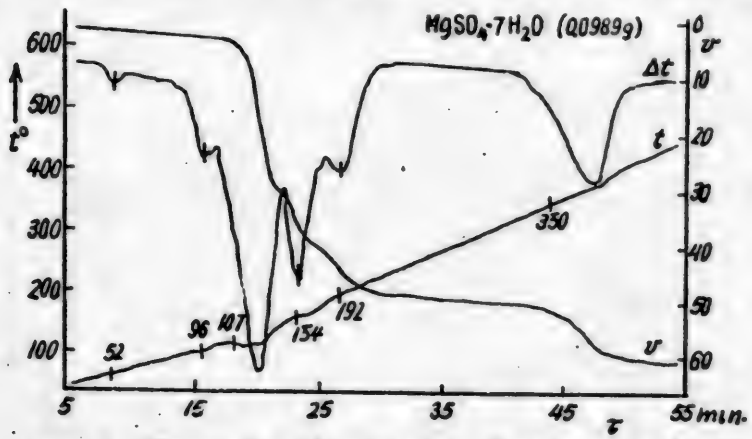



Figure 5. Thermogram of sempthydrate of magnesium sulfate. v = degree of gasification

* N.P. Anoshina took the thermograms adduced.

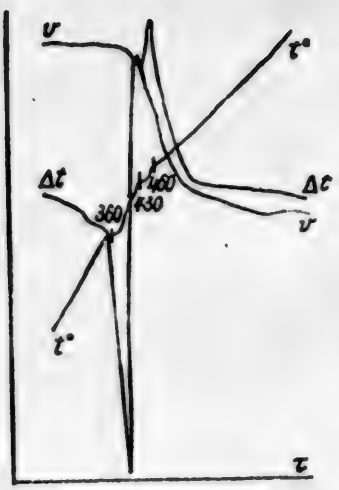



Figure 6 Thermogram of potassium chlorate
v – curve of oxygen liberation

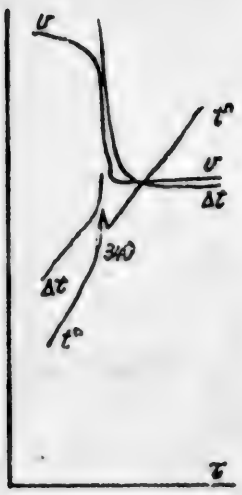



Figure 7 The same, but with manganese dioxide present.

200-350 when it is converted into the dehydrated form.

Another example of the use of this method is in a study of the thermal decomposition of certain oxygen-containing compounds.

Figure 6 illustrates the curves obtained when $KClO_3$ was heated alone while Figure 7 illustrates the curves obtained when the same material was heated with manganese dioxide as a catalyst. In the first instance the salt melted at a temperature of 360° and was accompanied by an endothermic effect after which decomposition with evolution of oxygen set in (exothermic effects at 430 and 460°). In the second instance a rapid decomposition of the salt started at 340° – which is lower than the melting point of the salt – and evolution of gas finished rapidly.

By measuring the volume of oxygen evolved by means of the photogram it is possible to determine the amount of chlorate in a sample even without preliminary separation from other components.

## SUMMARY

Examples which are given above show that the method suggested can find wide application in research laboratories for the study of various thermal processes.

It would also be very useful for studying many other processes involving the evolution of gas, e.g., electrochemical and biochemical processes, etc.

Finally, this method is also applicable for analytical purposes both for carrying out ordinary gas-volumetric analysis and in particular for quantitative phase analysis.

## LITERATURE CITED

[1] N. S. Kurnakov, J. Russ. Phys. Chem. Soc., 36, 841 (1904)

[2] L. G. Berg, A. V. Nikolaev and E. Ya. Rode, "Thermography" USSR Acad. Sci. Press, 1944.

[3] L. G. Berg and V. Ya. Anosov, J. Gen. Chem., 12, 31 (1942)

[4] L. G. Berg, Factory Labs, 10, 1171 (1948)

[5] L. G. Berg and B. Ya. Tentelbaum, Proc. Acad. Sci. U.S.S.R., 79, 791 (1951).

Received September 9, 1953

# DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING SULFUR AND NITROGEN, IN THE PRESENCE OF CATALYSTS

P. N. Fedoseev and M. M. Pavlenko

The Nikolaev Ship Building and Pedagogic Institute

In our first communications [1,2] we indicated that organic compounds can be analyzed rapidly and accurately by using amorphous chromic oxide obtained by the decomposition of ammonium bichromate, as a catalyst in elemental organic analysis.

It was shown that the analysis can be carried out in an atmosphere of pure oxygen when its rate of flow is increased to 350 ml/minute without decreasing the accuracy of the method.

The adsorption of oxides of nitrogen outside the combustion tube by means of oxidizing agents was verified. The apparatus was considerably simplified and the time for analysis was cut by 8-10 times.

Organic compounds containing C, H, O and N were analyzed during the course of the work indicated above.

In the present article we shall describe a method for the analysis of organic compounds which contain S and halogens in addition to C, H, O and N.

When the oxygen rate was increased one would have expected that some of the halogens and sulfur would escape into the absorption apparatus. Our experiments showed that a layer of metallic silver 10 cm long (weight 6-7 g) completely absorbed sulfur oxides and halogens when using a 10-12 mm diameter tube at 650-750°. Lead chromate could be used instead of silver but the layer thickness had then to be increased to 20 cm.

Certain complications arise when organic compounds containing halogens are analyzed. When such compounds are analyzed the results for carbon are, as a rule, one, two, or even more percent lower than the theoretical value, according to how much halogen is present. The greater the halogen content the worse the results.

Halogens do not affect the accuracy of hydrogen determinations. It must be noted however that when fresh catalysts are used for the analysis of organic compounds containing halogens the results are completely satisfactory. Subsequent analysis with the same catalyst gives low results for carbon. Nevertheless, since the catalyst is easily prepared and is cheap and easily available, while refilling the tube does not present any difficulties or take a long time, in individual cases where the halogen content is low it is possible to analyze the organic compound containing halogens by our method in which the catalyst is changed after each determination.

Coal, petroleum, fuel oil, oils and other technical products can be successfully analyzed using our method.

## EXPERIMENTAL

The tubes were filled as follows (Fig. 1).

A small asbestos stopper was placed at a distance of 40-50 mm from the end of the tube and then a layer of metallic silver ca. 100 mm long and a 150 mm layer of granular chromic oxide kept in position by asbestos plugs. The silver was in the form of gauze, or packed narrow ribbon (1-2 mm wide) or wire, etc.

## ANALYTICAL PROCEDURE

The freshly filled combustion tube was heated for 2-3 hours in a stream of oxygen.

When the tube was not in use it was sealed with a calcium chloride tube; before using, a stream of dry oxygen was passed for 10-20 minutes through the tube connected to the absorption apparatus. The

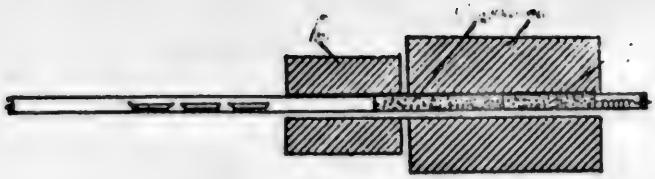


Fig. 1.

apparatus was then disconnected and transferred to the balance room, where it was kept for 15-20 minutes before weighing.

The sample, varying in weight from 0.06 to 0.30 was arranged in one or more boats according to the amount taken and the character of the substance analyzed. The contents of the tared boats were covered with calcined chromic oxide from a sealed tube.

Two electric furnaces were used for heating, the larger one A was 250-300 mm long while B, the smaller was 150-180 mm. The temperature of the large oven was kept at 700-750° all the time.

The second small furnace served for igniting the substance and for calcining the empty tube, it should therefore heat and cool rapidly. This furnace should be movable. The small oven was fitted on after introducing the sample in the boat into the tube. When the absorption apparatus had been connected and the sample introduced the small furnace heated up to 700-800° was moved up. The furnace was moved up to the boat containing the substance so as to cover $\frac{1}{3} - \frac{1}{2}$ of the length of the boat. When this had been done the oxygen rate was increased to 150-200 ml/minute. When the substance had been ignited the furnace was moved back and, when necessary (red sooty flame) the oxygen flow increased to 250-300 ml/minute.

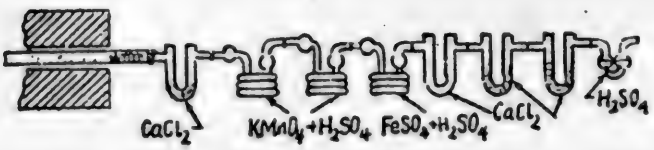



Fig. 2.

When all the substance in the first boat had been burnt the substance in the second boat was treated likewise. The time taken for ignition was 1-3 minutes according to the amount and nature of the test substance. Finally the tube was heated for 5-10 minutes with the oxygen still running after which analysis could be considered complete. The apparatus was disconnected, and weighed, and the percentage of carbon and hydrogen calculated.

Anhydrous calcium chloride was used for absorbing water, while ascarite or lumps of KOH were used for trapping $CO_2$. When compounds which contained sulfur and nitrogen in addition to carbon and hydrogen were analyzed, 1-3 traps containing an oxidizing mixture, and one trap containing a saturated solution of ferrous salt (ferrous sulfate) in 30% $H_2SO_4$ were placed after the water absorption train (Fig. 2)

Concentrated $H_2SO_4$ must be used for preparing the oxidizing mixture. Concentrated $H_2SO_4$ was distilled and the first one third laid aside, the other two-thirds of the distillate was collected and stored in a bottle fitted with a ground glass stopper. The 0.25% solution of $KMnO_4$ was prepared in concentrated $H_2SO_4$.

Examples of the results obtained for the analysis of organic compounds, coal and peat containing sulfur and halogens are given in Tables 1 and 2.

We wish to express our thanks to the Chief of the Fuel Laboratory of the F. E. Dzerzhinsky All-Union Scientific Thermotechnical Institute, T. A. Zikeev, for his gift of a number of samples of fuel and for his continued interest in our work.

## SUMMARY

1. A method is described for the quantitative determination of C and H in organic compounds containing sulfur and nitrogen.

TABLE 1

| No. | Substance | Calculated in % | | Found in % | | Δ in % | |
|---|---|---|---|---|---|---|---|
| | | C | H | C | H | C | H |
| 1 | Sulfosalicylic acid | 33.09 | 3.95 | 33.04 | 3.99 | −0.05 | + 0.03 |
| | | 33.09 | 3.95 | 32.97 | 4.10 | −0.12 | + 0.14 |
| 2 | p-Toluene sulfamide | 49.11 | 5.30 | 49.32 | 5.31 | + 0.21 | + 0.01 |
| | | 49.11 | 5.30 | 49.27 | 5.32 | + 0.16 | + 0.02 |
| 3 | Bis(1,1-dimethylpentene-3-one-sulfide) | 66.13 | 8.72 | 66.26 | 8.57 | + 0.13 | −0.15 |
| | | 66.13 | 8.72 | 66.08 | 8.71 | −0.05 | −0.01 |
| 4 | Sulfanilic acid | 41.60 | 4.07 | 41.53 | 4.11 | −0.07 | +0.04 |
| | | 41.60 | 4.07 | 41.67 | 4.17 | +0.07 | + 0.10 |
| 5 | Naphthenic acids | 51.71 | 4.34 | 51.82 | 4.39 | + 0.11 | + 0.05 |
| | | 51.71 | 4.34 | 51.79 | 4.43 | + 0.08 | + 0.09 |
| 6 | Diphenylthiourea | 68.39 | 5.30 | 68.34 | 5.26 | −0.05 | −0.04 |
| | | 68.39 | 5.30 | 68.38 | 5.35 | −0.01 | +0.05 |
| 7 | Thiosemicarbazide | 13.18 | 5.53 | 13.36 | 5.46 | + 0.18 | −0.07 |
| | | 13.18 | 5.53 | 13.24 | 5.49 | + 0.06 | −0.04 |
| 8 | Chlorobenzene • | 64.06 | 4.48 | 64.03 | 4.21 | −0.03 | −0.27 |
| | | 64.06 | 4.48 | 64.15 | 4.38 | + 0.09 | −0.10 |
| 9 | Bromocamphor • | 51.96 | 6.54 | 51.97 | 6.32 | + 0.01 | −0.22 |
| | | 51.96 | 6.54 | 51.71 | 6.76 | − 0.25 | +0.22 |
| 10 | m-Nitrochlorobenzene • | 45.72 | 2.54 | 43.83 | 2.71 | −1.89 | + 0.17 |
| | | 45.72 | 2.54 | 42.51 | 2.50 | −3.21 | −0.04 |
| 11 | p-Dichlorobenzene • | 49.03 | 2.72 | 47.12 | 2.74 | −1.91 | + 0.02 |
| | | 49.03 | 2.72 | 46.98 | 2.69 | −2.05 | − 0.04 |

2. It has been shown that the method is applicable to the analysis of various types of organic materials containing carbon, hydrogen, nitrogen and sulfur.

3. It has been shown that the method can be applied to the analysis of fuels.

4. By using a large combustion tube it is possible to analyze large samples by distributing the sample among more than one boat. This may prove to be very useful when the test substance contains only a very small amount of carbon and hydrogen.

5. The method has been simplified considerably; the time required for an analysis has been reduced 8-10 times without decreasing the accuracy of carbon and hydrogen determinations.

6. This gives us grounds for hoping that this method will find wide application in various research, factory, and college laboratories.

Received March 15th 1951

• Fresh catalyst.

TABLE 2

| Test No. | Fuel tested | $W_t$ | $A_d$ | $S^{dry}_{tot.}$ | $V_f$ | % $C_t$ | | Diff. | % $H_t$ | | Diff. | Observations |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | VTI | NKI | | VTI | NKI | | |
| 1 | Chinese coal | 0.59 | – | 5.51 | 14.71 | 76.16 | 76.04 | −0.12 | 3.56 | 3.57 | +0.01 | Analysis checked |
| | | 0.59 | – | 5.51 | 14.71 | 76.16 | 75.81 | −0.35 | 3.56 | 3.68 | +0.12 | in VTI(No.6466) |
| 2. | Brown coal dust | 6.56 | – | 1.68 | 39.59 | 52.39 | 52.24 | −0.15 | 3.27 | 3.06 | −0.21 | Ditto |
| | | 6.56 | – | – | 39.59 | 52.39 | 52.74 | +0.35 | 3.27 | 3.11 | −0.16 | No. 6545 |
| 3. | Coal (anthracite) | 1.99 | – | 2.80 | 3.96 | 74.91 | 75.03 | +0.12 | 1.41 | 1.33 | −0.08 | Ditto |
| | | 1.99 | – | 2.80 | 3.96 | 74.91 | 75.18 | +0.27 | 1.41 | 1.38 | −0.03 | No. 6491 |
| 4. | Peat | 11.46 | – | 0.38 | – | 45.74 | 46.08 | +0.34 | 4.72 | 4.46 | −0.26 | Ditto |
| | | 11.46 | – | 0.38 | – | 45.74 | 45.85 | +0.11 | 4.72 | 4.73 | +0.01 | No. 5986 |
| 5. | Intermediate product | 0.70 | 16.08 | – | 20.78 | 72.52 | 72.50 | −0.02 | 3.95 | 3.89 | −0.06 | Ditto |
| | | 0.70 | 16.08 | – | 20.78 | 72.52 | 72.58 | +0.06 | 3.95 | 3.91 | −0.04 | No. 5834 |
| 6. | Coal "T" | 0.99 | 22.93 | 2.93 | 8.11 | 68.74 | 68.57 | −0.17 | 2.43 | 2.41 | −0.02 | Ditto |
| | | 0.99 | 22.93 | 2.93 | 8.11 | 68.74 | 68.36 | −0.38 | 2.43 | 2.48 | +0.05 | No. 5617 |
| 7. | Coal | 0.59 | 6.90 | 0.98 | 14.61 | 83.45 | 83.66 | +0.21 | 4.07 | 4.06 | −0.01 | Ditto |
| | | 0.59 | 6.90 | 0.98 | 14.61 | 83.45 | 84.09 | +0.64 | 4.07 | 4.08 | +0.01 | No. 5640 |
| 8. | Anthracite "ARSh" | 2.83 | 17.25 | 1.93 | 3.88 | 75.28 | 75.49 | +0.21 | 1.32 | 1.30 | −0.02 | Ditto |
| | | 2.82 | 17.25 | 1.93 | 3.88 | 75.28 | 75.23 | −0.05 | 1.32 | 1.34 | +0.02 | No. 5644 |
| 9. | Moscow Coal | 8.00 | 34.04 | 3.48 | 50.06 | 40.99 | 40.82 | −0.17 | 3.24 | 3.16 | −0.08 | Ditto |
| | | 8.00 | 34.04 | 3.48 | 50.06 | 40.99 | 40.79 | −0.20 | 3.24 | 3.15 | −0.09 | No. 5771 |
| 10. | Silesian Coal | 5.86 | 18.82 | 2.23 | 38.21 | 59.00 | 59.10 | +0.10 | 3.88 | 3.70 | −0.18 | Ditto |
| | | 5.86 | 18.82 | 2.23 | 38.21 | 59.00 | 59.02 | +0.02 | 3.88 | 3.79 | −0.09 | No. 5753 |

Notes.

VTI – The F. E. Dzerzhnisky All-Union Scientific Research Institute.

NKI – The S. O. Makarov Nikolaev Ship-Building Institute.

$W_t$ – moisture content of test material in %.

$A_d$ – ash in the dry fuel in %

$S^{dry}_{tot.}$ – total sulfur in the dry mass, in %.

$V_f$ – volatile material in the fuel, in %.

$C_t$ – carbon in the test material, in %.

$H_t$ – hydrogen in the test material, in %.

## LITERATURE CITED


[1] P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem., 5, 296 (1950).

[2] P. N. Fedoseev and M. M. Pavlenko, J. Anal. Chem., 6, 317 (1951).

[3] M. O. Korshun and N. E. Gelman, "New methods of Elemental Microanalysis", State Chem. Press, 1949.

[4] M. O. Korshun and V. A. Klimova, J. Anal. Chem., 4, 292 (1949).

[5] M. O. Korshun and V. A. Klimova, J. Anal. Chem., 3, 176 (1948).


Received March 15, 1951

# THE BEHAVIOR OF CERTAIN CATIONS DURING THE COMPLEXOMETRIC DETERMINATION OF WATER HARDNESS

T. B. Styunkel, E. M. Yakimets, and D. A. Savinovsky

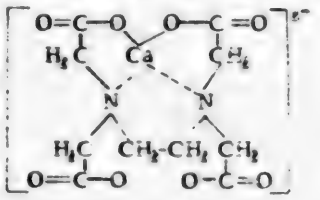
The S. M. Kirov Ural Polytechnic Institute

During the last six months the oleate method for the determination of water hardness has been completely superseded by a complexometric method at the Ural Electric Power Stations [1]. This method is based on the interaction between calcium and magnesium ions with the dibasic sodium salt of ethylenediaminetetracetic acid, also called Trilon B. This reaction leads to the formation of colorless inner complex compounds which are readily soluble in water.

If the ethylenediaminetetracetate ion be denoted by $R^{4-}$, the reaction of its bivalent salt with calcium ions (or magnesium) can be represented by the following schematic equation:

$$Ca^{2+} + Na_2H_2R = Na_2[CaR]^{2-} + 2H^+,$$

where the inner complex ion $[CaR]^{2-}$ has the structure [2]

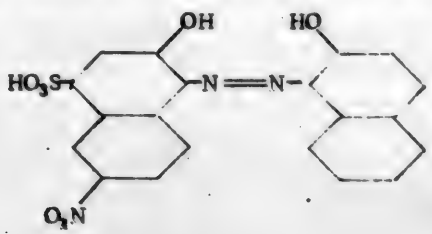


The instability constant of the complex ion is $K = \frac{c_{Ca^{2+}} \cdot c_{R^{4-}}}{c_{CaR^{2-}}} = 2.6 \cdot 10^{-11}$, while for magnesium $K = \frac{c_{Mg^{2+}} \cdot c_{R^{4-}}}{c_{MgR^{2-}}} = 2.0 \cdot 10^{-9}$.

Trilon B also gives similar soluble inner complex compounds with a number of other cations ($Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$ etc.), [3].

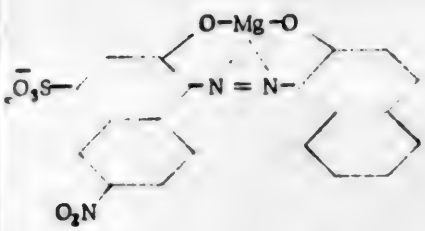
The technique of determining water hardness by complexometric methods is based on extraction of calcium and magnesium ions from their compounds with organic dyes by means of Trilon B; the dyes have different colors in the presence and in the absence respectively of calcium and magnesium ions at a definite pH value. One of the dyes recommended in the literature is Eriochrome Black T [4] which is manufactured in Russia under the trademark "Chromogen Black special ET-00"; while we have suggested two dyes, also produced in Russia which possess functional-analytical groups similar to those of Eriochrome Black T; these are Acid Chrome Blue K and Acid Chrome Dark Blue [5,10]. Very little has been said in the literature about the reaction mechanism between the dyes indicated above and calcium and magnesium ions; there are only formal indications of the character of the color change of the dye in alkaline media upon the addition of solutions containing calcium and magnesium salts.

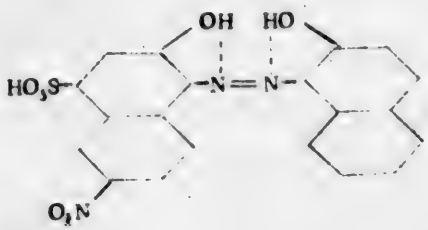
Chromogen Black, special ET-00, is a monoazo dye with a structural formula:



In alkaline media, in the presence of calcium and magnesium ions and in acid media, the dye is colored wine-red.

We postulate that in both cases we have the phenomenon of inner complex formation via the calcium and magnesium ions in alkaline media and through the hydrogen ion in acid media:



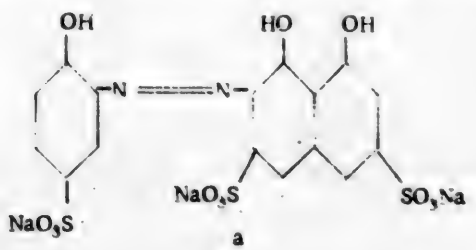

A similar mechanism can also be postulated in the case of the other two indicators mentioned above. The color of the dye in alkaline media in the presence of calcium and magnesium ions and in acid media is red in each case, while the color is violet in alkaline media not containing calcium and

TABLE 1

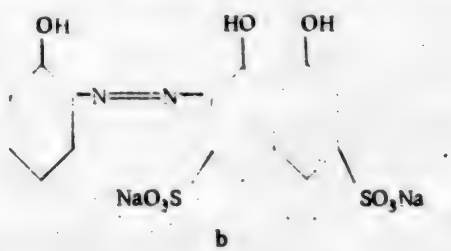
Sensitivity of the Indicators to Various Cations

| Cation examined and pH of the solution | | Concentration of Cation Detected by the Indicator | | | | | |
|---|---|---|---|---|---|---|---|
| | | Milli-equivs / liter | | | g/mml | | |
| | | Chromogen Black ET-00 | Acid Chrome Blue K | Acid Chrome Dark Blue | Chromogen Black ET00 | Acid Chrome Blue K | Acid Chrome Dark Blue |
| $Ca^{2+}$ | 9.8 | $7 \cdot 10^{-4}$ | $7 \cdot 10^{-4}$ | $7 \cdot 10^{-3}$ | $1.4 \cdot 10^{-5}$ | $1.4 \cdot 10^{-7}$ | $1.4 \cdot 10^{-7}$ |
| $Mg^{2+}$ | 9.8 | $7 \cdot 10^{-5}$ | $1.5 \cdot 10^{-4}$ | $1.5 \cdot 10^{-4}$ | $8.4 \cdot 10^{-6}$ | $2.0 \cdot 10^{-6}$ | $2.0 \cdot 10^{-6}$ |
| $Zn^{2+}$ | 9.8 | $3.6 \cdot 10^{-3}$ | $3.5 \cdot 10^{-3}$ | $3.5\ 10^{-3}$ | $1.1 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ |
| $Mn^{2+}$ | 9.8 | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-3}$ | $1.1 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ |
| $Cu^{2+}$ | 9.8 | $7 \cdot 10^{-5}$ | $3.5 \cdot 10^{-3}$ | $3.5 \cdot 10^{-5}$ | $2.0 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ |
| $Ca^{2+}$ | 12.3 | $2.8 \cdot 10^{-2}$ | $7 \cdot 10^{-5}$ | $7 \cdot 10^{-5}$ | $5.6 \cdot 10^{-7}$ | $1.4 \cdot 10^{-7}$ | $1.4 \cdot 10^{-7}$ |
| $Mg^{2+}$ | 12.3 | $1.7 \cdot 10^{-3}$ | $1.7 \cdot 10^{-5}$ | $1.7 \cdot 10^{-5}$ | $2.0 \cdot 10^{-5}$ | $2.0 \cdot 10^{-6}$ | $2.0 \cdot 10^{-6}$ |
| $Zn^{2+}$ | 12.3 | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-5}$ | $1.1 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ |
| $Mn^{2+}$ | 12.3 | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-5}$ | $3.5 \cdot 10^{-5}$ | $1.0 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ | $1.0 \cdot 10^{-7}$ |
| $Cu^{2+}$ | 12.3 | $7.0 \cdot 10^{-3}$ | $3.5 \cdot 10^{-3}$ | $3.5 \cdot 10^{-5}$ | $2.2 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ | $1.1 \cdot 10^{-7}$ |

magnesium ions. The structural formulas of Acid Chrome Blue K (a) and Dark Blue (b) are as follows

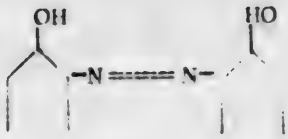



a




b

The color of the indicator in alkaline media in the presence of calcium and magnesium ions and in acid media in their absence is rose while in alkaline media in the absence of calcium and magnesium ions, the color is bluish-grey. The characteristic group in all three dyes is not specific for calcium and magnesium ions.



We experimentally determined the sensitivity of the three indicators toward calcium, magnesium, zinc, copper, and bivalent manganese (in the presence of reducing agents). The results are given in Table 1.

Table 1 shows that the three dyes are highly sensitive in alkaline media to $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Cu^{2+}$. The sensitivity of Chromogen Black ET-00 to calcium and magnesium depends markedly on the pH of the test; it increases with increasing pH from 9.8 to 12.3.

The possibilities of determining the cations mentioned above in the presence of one of the three indicators by binding them into inner complex anions with Trilon B, depends on the ratios of the instability constants of the complex ions formed by a given cation with the indicator and with Trilon B respectively. The nature of the effect of the cations indicated, and the results for the determination of water hardness by a complexometric method, also depend on these ratios. The cations most likely to be present in the natural or processed water are $Fe^{2+}$, $Fe^{3+}$, followed by $Al^{3+}$, $Mn^{2+}$, $Zn^{2+}$, $Cu^{2+}$.

Zinc ions form (Table 1) red complexes with dyes and are quantitatively extracted from them by Trilon B, i.e., the instability constants of the inner complex ions of zinc with the dyes are greater than the instability constants of the inner complex anions formed between zinc and Trilon B.•

When water hardness is being determined, Zn will therefore be titrated with Trilon B in the same way as Ca and Mg so that the results will be higher by an amount equal to the Zn content. Zn is quantitatively determined by Trilon B in the presence of one of the indicators described (Table 2).

The behavior of Mn ions in complexometric methods of determining water hardness may be characterized as follows. After the addition of a buffer solution and indicator to a test sample containing $Mn^{2+}$, the red color which originally develops gradually becomes paler and the solution becomes eventually colorless. The explanation is probably as follows: in alkaline media, the most stable valencies of Mn are +3 and +4 [7]. $Mn^{2+}$ ions are easily oxidized at a pH of 9-12 by oxygen dissolved in the water and difficultly soluble hydroxides of tri- and quadrivalent manganese, which adsorb the dye, are formed.

The addition of a reducing agent such as a solution of hydroxylamine hydrochloride to the test sample allows the manganese to remain in the test solution as $Mn^{2+}$ ions which give red complexes with the indicator. Trilon B extracts $Mn^{2+}$ quantitatively from these complexes which means that the instability constant of the inner complex ions of $Mn^{2+}$ with the indicator is greater than the instability constant of the complex ion formed between $Mn^{2+}$ and Trilon B.•• $Mn^{2+}$ is quantitatively determined on titration with Trilon B in the presence of the indicators enumerated above; consequently it interferes during the determination of water hardness by complexometric methods and leads to high results.

TABLE 2

Results of the Determination of Zinc with Trilon B

| Conc. of $Zn^{2+}$ in test material in mg/l | $Zn^{2+}$ found mg/l |
|---|---|
| 11.7 | 11.65 |
| 7.02 | 7.02 |
| 5.85 | 5.9 |
| 3.51 | 3.49 |
| 1.17 | 1.15 |
| 0.58 | 0.58 |

$Cu^{2+}$ ions also (Table 1) form red complexes with dyes. A test solution containing $Cu^{2+}$, a buffer, and dye remains red even when Trilon B is added. If the reagents are added together in the reverse order, i.e., if the dye is added to the test solution containing $Cu^{2+}$ ions, Trilon B, and a buffer, then the test solution remains blue. The only possible explanation for this is that the values of the instability constants of the complexes formed between $Cu^{2+}$ ions and the indicator and Trilon B••• respectively, are similar.

$Cu^{2+}$ will accordingly not titrate with Trilon B but the determination of water hardness in the presence of $Cu^{2+}$ is impossible because there is no transition point for the indicator.

• The instability constant of the complex zinc-Trilon B is $7.1 \cdot 10^{-1}$ [9].

•• The instability constant of the complex ion formed between Trilon B and $Mn^{2+}$ is $3.4 \cdot 10^{-14}$ [9].

••• The instability constant of the complex ion formed between Trilon B and $Cu^{2+}$ is $4.1 \cdot 10^{-19}$ [9].

TABLE 3

Results of Determination of $Mn^{2+}$ with Trilon B in Presence of Hydroxylamine Hydrochloride

| Conc. of $Mn^{2+}$ in test material in mg/l | $Mn^{2+}$ found, mg/l |
|---|---|
| 0.1 | 0.15 |
| 0.2 | 0.21 |
| 0.4 | 0.43 |
| 0.6 | 0.65 |
| 0.8 | 0.82 |
| 1.0 | 1.04 |

TABLE 4

Results of the Determination of Total Hardness in the Presence of $Zn^{2+}$ and $Cu^{2+}$

| Water hardness, in degrees | Amount present in, mg/l | | Amount of 10% solution of $Na_2S$ added | Hardness determined, in degrees |
|---|---|---|---|---|
| | $Cu^{2+}$ | $Zn^{2+}$ | | |
| 10 | 0.5 | | – | Transition point absent |
| 10 | 0.5 | | 1 | 10 |
| 1 | 0.5 | | 1 | 1 |
| 0.2 | 0.5 | | 1 | 0.2 |
| 0.05 | 0.5 | | 1 | 0.05 |
| 10 | – | 7 | – | 11.1 |
| 10 | | 7 | 1 | 10.0 |
| 0.2 | | 5 | 1 | 0.2 |
| 0.05 | | 1 | 1 | 0.05 |

$Al^{3+}$ ions at concentrations up to 20 mg/liter do not affect hardness determinations. $Fe^{2+}$ ions on addition of a buffer solution, i.e., in alkaline media are rapidly oxidized by dissolved oxygen to $Fe^{3+}$, so that it is always $Fe^{3+}$ ions which have to be dealt with during water hardness estimations by complexometric methods. Water hardness can be determined in the presence of up to 10 mg/liter iron. The end point can be clearly detected though the brown color of the ferric hydroxide distorts the blue color of the dye.

Interference from $Fe^{3+}$ and $Al^{3+}$ can be eliminated by diluting the test solution with distilled water till the concentration is below 10 mg/liter for $Fe^{3+}$ and less than 20 mg/liter for $Al^{3+}$

This method is no good for $Cu^{2+}$, $Zn^{2+}$ and $Mn^{2+}$, because they interfere at very low concentrations. Interference on the part of these elements can be eliminated by combining them into stable complexes or precipitating them in the form of difficultly soluble compounds.

The most insoluble compounds of copper and zinc are the sulfides whose solubility products are $8.5 \cdot 10^{-45}$ and $7.9 \cdot 10^{-26}$, respectively [6].

Since the solubility of these sulfides is very low, Trilon B will not extract $Cu^{2+}$ and $Zn^{2+}$ from them, so that water hardness can be determined with Trilon B in the presence of the sulfide precipitates without any preliminary filtration of the sulfides. We are of course dealing with interference from low concentrations of $Zn^{2+}$ and $Cu^{2+}$ when determining water hardness, so that any sulfides formed are either colloidally dispersed or form only a small amount of precipitate.

In such a case, the addition of 1 ml of 5-10% sodium sulfide to the test solution before addition of the buffers and the indicator completely eliminates interference from $Cu^{2+}$ and $Zn^{2+}$ (Table 4).

Interference from $Mn^{2+}$ can be eliminated by addition of hydroxylamine hydrochloride. In this case, titration is normal but the hardness will be the sum of $Mn^{2+}$, $Ca^{2+}$ and $Mg^{2+}$.

The amount of $Mn^{2+}$ in natural water does not exceed 0.5 mg/l [9] so that its presence will have practically no effect on the results.

## SUMMARY

1. The behavior of Ca, Mg, Zn, Mn, Cu, Al, Fe during the complexometric determination of water hardness with Trilon B in the presence of the indicators – Chromogen Blue ET-00, Acid Chrome Blue, and Acid Chrome Dark Blue, has been considered.

2. Methods for eliminating interference from the various cations have been indicated.

Received April 28th 1952

## LITERATURE CITED

[1] D. A. Savinovsky, T. B. Styunkel and E. M. Yakimen, Bull., F. E. Dzerzhnisky All-Union Scientific Research Institute, 21, 2, 26 (1952).

[2] K. V. Astakhov, E. D. Kiseleva, J. Gen. Chem., 20, 10, 1780 (1950).*

[3] G. Schwarzenbach, A. Willi, R. Bach, Helv. Chim. Acta, 30, 1303 (1947).

[4] G. Schwarzenbach, E. Riedermann, Helv. Chim. Acta, 31, 56-58 (1948).

[5] D. A. Savinovsky, T. B. Styunkel and E. M. Yakimen, Bull., F. E. Dzerzhnisky All-Union Scientific Research Institute, 21, 3, 22 (1952).

[6] Yu. Yu. Lurye, "Calculations and Reference Tables for Chemists", Moscow-Leningrad, State Chem. Press, 1947, pp. 103, 105.

[7] S. T. Orlovsky, J. Russ. Chem. Soc., 61, 7, 1185 (1929).

[8] V. A. Klyachko, A. A. Kastalsky "Purification of Water for Industrial Purposes", Moscow, State Construct. Press., 1950, p. 295.

[9] G. Schwarzenbach, E. Freitag, Helv. Chim. Acta, 34, 1503 (1951).

[10] V. I. Kuznetsov, J. Anal. Chem., 5, 367 (1950) V. I. Kuznetsov, Prog. Chem., XVIII, 75, (1949), L. M. Kulberg, "Organic Reagents in Analytical Chemistry" State Chem. Press, 1951.

---

* See Consultation Bureau Translation page 1841.

# MICROCRYSTALLOSCOPIC REACTIONS FOR CYANIDES

I. M. Korenman and A. A. Belyakov

The Gorky Scientific-Research Institute for Industrial Hygiene

The reaction based on formation of a precipitate of silver cyanide is the best of the characteristic and sensitive microcrystalloscopic reactions for cyanides. The amorphous precipitate which is initially formed is recrystallized from concentrated nitric acid or is treated with ammonia until it dissolves; according to the amount of ammonia which evaporates fine crystals of silver cyanide fall out. When this reaction is carried out in a gas cell fine crystals of silver cyanide are formed. Coarse crystals of silver cyanide are obtained when precipitation is carried out from more concentrated solutions of cyanides, in such cases the cyanide anion content should not be less than 5μg [1].

Organic reagents of high sensitivity and specificity [2], are widely used in qualitative and quantitative analyses. Benzidine in the presence of cupric acetate which forms a blue crystalline precipitate of the oxidation products of benzidine with cyanide solution is one of the organic reagents used for microreactions for cyanides. Similar precipitates are given by tolidine, dianisidine and hydrocerulignone [3]. These reactions are not specific, since they also form crystalline precipitates in the presence of oxidizing agents ($Cr_2O_7^{2-}$, $MnO_4^-$ etc.). Recently metal-organic compounds have started coming into use as reagents (triphenyltin chloride, mercury succinimide, and benzidine etc). [4].

During a study of the analytical properties of certain mercuriated aromatic amino compounds we established that they could be used as analytical reagents for anions. These compounds form characteristic crystalline precipitates with various anions and by a study of crystal form and certain other crystallooptical constants the presence or absence of certain anions can be determined. The reactions which occur between mercury organic compounds and the anions proceed as follows

$$RHgAc + X^- \rightarrow RHgX + Ac^-,$$

where $X^-$ is the anion to be detected, while $Ac^-$ is the acetate anion. By means of the crystalline precipitates formed by interaction with these mercury organic compounds (2) microgram quantities and fractions of a microgram of the test anion can be detected in a drop of solution. The present article is the result of our studies on microcrystalloscopic reactions between certain mercury organic compounds and cyanides. 20 mercury organic compounds prepared by mercuriating aromatic amino compounds by methods indicated in the literature [5] were tested.

Of the compounds tested by us the following gave crystalline precipitates with cyanides:

1, 4 - aminophenylmercuryacetate $NH_2C_6H_4HgAc$.
1, 4 - ethylaminophenylmercuryacetate $(C_2H_5)NH{\cdot}C_6H_4HgAc$.
1, 4 - dimethylaminophenylmercuryacetate $(CH_3)_2N{\cdot}C_6H_4HgAc$.
1, 4 - ethylbenzylaminophenylmercuryacetate $(C_6H_5)(C_2H_5CH_2)N{\cdot}C_6H_4HgAc$
1, 4 - diethylaminophenylmercuryacetate $(C_2H_5)_2N{\cdot}C_6H_4HgAc$.
3 - methyl - 4, 1 - aminophenylmercuryacetate $CH_3(NH_2)C_6H_3HgAc$.
3 - nitro - 1, 4-aminophenylmercuryacetate $NO_2(NH_2)C_6H_3HgAc$.
1, 2 - toluidine - 4 6 - dimercuryacetate $CH_3(NH_2)C_6H_2(HgAc)_2$

The experimental procedure was as follows: a drop of the test cyanide solution was placed on an object glass together with a drop of freshly prepared saturated solution of the mercury organic compound in water or in 5-10% acetic acid, and the formation of a crystalline precipitate observed under the microscope. The compounds listed with the exception of 1, 2 - toluidine - 4, 6 - dimercuryacetate form crystalline precipitates also with $Cl^-$, $Br^-$, $I^-$, $CNS^-$ and with some other anions, so that in the presence of these anions the reactions for cyanide are not specific. In order to increase the specificity, the reactions were carried out in a gas cell. However, even under these conditions some of the reagents listed were still inapplicable. Thus, 1, 4 - dimethylaminophenylmercuryacetate gave a comparatively highly sensitive reaction for cyanides in solution (0.1 g CN) but did not give a crystalline precipitate in the gas cell, while 3 - nitro - 1,

4 - aminophenylmercuryacetate though capable of forming a crystalline precipitate in the gas cell can only detect CN if the latter is present in amounts of not less than 1 μg $CN^-$.

Three compounds, viz. 1 4 - ethylbenzylaminophenylmercuryacetate 1 4 - dimethylaminophenylmercuryacetate, and 1, 2 - toluidine - 4 6 - dimercuryacetate form crystalline compounds both with dilute solutions of cyanides and with small amounts of cyanides in a gas cell, and can therefore be used for the specific detection of $CN^-$.

The table below includes some of the results characterizing the crystalline precipitates which are formed by the interaction of cyanide solutions (without the use of a gas cell) with these three compounds.

TABLE

| Reagent | 1,4-ethylbenzylamino-phenylmercuryacetate $(C_2H_5)$-$(C_6H_5CH_2)N$-$C_6H_4HgAc$ | 1,4-dimethylaminophenyl-mercuryacetate $(CH_3)_2N$-$C_6H_4HgAc$ | 1,2 toluidine-4,6-dimercuryacetate $CH_3(NH_2)C_6H_2(HgAc)_2$ |
|---|---|---|---|
| Composition of precipitate | $(C_2H_5)(C_6H_5CH_2)N$-$C_6H_4HgCN$ | $(CH_3)_2N$-$C_6H_4HgCN$ | $CH_3(NH_2)C_6H_2(HgCN)_2$ |
| Crystal form | Plate, rosettes | Plates, rosettes, rods | rosettes in the form of snow flakes |
| Limit of identification in μg | 0.25 | 0.25 | 0.25 |
| Maximum crystal size in μ | 140 | 90 | 120 |
| Pleochroism | Intense, yellow, red, green | Intense, yellow, red green | Weak yellow, blue |
| Extinction angle of crystal | 5 7 | 35 37 | 90 |

When the reactions are carried out in a gas cell the sensitivity increases and excess of other ions do not interfere appreciably. Only $S^{2-}$ seems to have a strong effect. If the amount of $S^{2-}$ exceeds that of the $CN^-$ ions in the test solution, then the reaction must be modified somewhat. To a drop of the test solution on the bottom of a gas cell, a drop of a 10-15% solution of lead acetate was added; the effect of the $S^{2-}$ was thus eliminated, and the solution was then mixed with a drop of 10% acetic acid. The cell was sealed with a cover glass, on the lower surface of which a small drop of reagent solution had been placed, after which the cell was mounted on the microscope object stage. The formation of precipitate crystals was observed in the upper drop using a small stop. The time which the reaction took did not exceed 10 minutes.

An acetic acid solution of 1, 4 -ethylbenzylaminophenylmercuryacetate forms a crystalline precipitate consisting of colorless or pale yellow rosettes and plates of up to 240 μ in size (Figure 1) with cyanides in a gas cell.* The limit of identification is 0.25 μg $CN^-$ while the limiting concentration is 1:8,000. Limiting ratios (at 0.25μg$CN^-$) are :

$CN^-$:$Cl^-$ (or $Br^-$) = 1:80
$CN^-$:$Fe(CN)_6^{4-}$ (or $Fe(CN)_6^{3-}$) = 1:65.
$CN^-$:$CNS^-$ (or $I^-$) = 1:40
$CN^-$:$S^{2-}$ (or $SO_3^{2-}$) = 1:35;
$CN^-$:$NO_3^-$ = 1:10.

The reagent crystals which are precipitated at the edges of the drop of reagent solution differ appreciably from crystals of the cyanide precipitate. The reagent crystals form colorless parallelograms which exhibit intense pleochroism; the angle of extinction is 35-37° while the acute angle of the parallelogram is 70°. (Figure 2). It is essential to note that the drop dries out very slowly in the gas cell and the appearance of reagent crystals can only be observed on removal of the drop from the cell.

1,4-Dimethylaminophenylmercuryacetate in aqueous or acetic acid solution reacts with cyanides in the gas cell to form colorless crystalline precipitates consisting of plates, rods, and rosettes, with sizes up to 55μ in aqueous solution (Figure 3) and up to 500μ in acetic acid solution (Figure 4). The limit of identification in aqueous solution is 0.03μg $CN^-$ while the limiting concentration is 1:65,000. The

* All the photographs were taken at a magnification of 100, Figure 3 at a magnification of 450. (See Plate, page 213.)

Limit of identification in acetic acid solution is 0.25 μg and the Limiting Concentration 1:8,000. The limiting ratios with other anions are the same as for reactions with 1,4-ethylbenzylaminophenylmercuryacetate, with the exception of reactions in the presence of $NO_2^-$ ions. The presence of a 35-fold excess of $NO_2^-$ as compared with $CN^-$ does not interfere with detection of $CN^-$. The reagent separates out in the form of bunches of fine colorless needles on drying out along the drop edges (Figure 5). The pleochroism of the reagent crystals is very weak, yellow-red and green; the extinction angle of the crystals is 16-19°.

1,2-toluidine-4,6-dimercuryacetate is a highly sensitive and specific reagent for cyanides, since in aqueous solution it does not form crystalline precipitates with any other anions except $CN^-$. This reagent can consequently be used for the detection of cyanides in solutions containing excess of other anions, and can be used with even greater success for the detection of cyanides in a gas cell. The precipitate crystals consist of colorless rosettes like snow-flakes with sizes up to 120μ (Figure 6). The Limit of identification for reactions carried out in a gas cell is 0.03μg $CN^-$ while the Limiting Concentration is 1:65,000. $S^{2-}$ interferes with the detection of $CN^-$ in solution. In such cases a drop of 10-15% lead acetate should be added to 3-4 drops of test solution. The solution is then centrifuged when it is ready for testing for $CN^-$. The limiting ratios when a gas cell is not used (for 0.25 μg of $CN^-$ are as follows:

$CN^-$ : $Cl^-$ (or $Br^-$, $I^-$, $SO_3^{2-}$) = 1:50.
$CN^-$ : $CNS^-$ (or $NO_2^-$) = 1:25
$CN^-$ : $FE(CN)_6^{3-}$ (or $Fe(CN)_6^{4-}$, $Fe(CN)_5NO^{2-}$) = 1:20.
$CN^-$ : $S^{2-}$ = 1:3

The limiting ratios for reactions carried out in a gas cell (for 0.03μg $CN^-$) $CN^-$ : $Cl^-$ (or $Br^-$, $I^-$, $CNS^-$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_5NO^{2-}$, $S^{2-}$) with addition of lead acetate = 1:50; $CN^-$ : $NO_2^-$ (or $SO_3^{2-}$) = 1:25; $CN^-$ : $S^{2-}$ without addition of lead acetate = 1:5. The reagent crystallizes out along the edges of reagent drops in the form of fine colorless rods and needles (Figure 7).

We tested 1,2-toludine-4,6-dimercuryacetate for the detection of cyanides in air and in certain organs of animals which had died from KCN poisoning.

If a drop of this reagent is placed on the inner wall of a gas cell containing 50 ml air with 1.2μg $CN^-$ crystals of the cyanide can be detected in the drop after 10 minutes. Under similar conditions $CN^-$ was detected in a liter of smoke from a certain type of tobacco and also when tests were made out under production conditions of galvanized baths containing KCN. By means of a gas cell technique we determined $CN^-$ in the liver and heart of a white rat poisoned with 2.5 mg KCN.

## SUMMARY


1. Three microcrystalloscopic reactions are proposed for the detection of $CN^-$ ions which are based on the formation of crystalline precipitates when 1,4-ethylbenzylaminophenylmercuryacetate, 1,4-dimethylaminophenylmercuryacetate, and 1,2-toluidine-4,6-dimercuryacetate respectively react with cyanides. Some crystallooptical constants are given for the crystals formed. The Limit of identification is 0.03 μg $CN^-$; it only takes 5-10 minutes to carry out a test.

2. 1,2-toluidine-4,6-dimercuryacetate is used for the detection of cyanides in solution. The Limit of identification is 0.25μg $CN^-$. With the exception of $S^{2-}$ interference from which can easily be eliminated by the addition of lead acetate, excess of $Cl^-$, $Br^-$, $CNS^-$, $NO_2^-$, $SO_3^{2-}$ do not appreciably affect the results.


## LITERATURE CITED


[1] I. M. Korenman, "Microcrystalloscopy" 177 (1947)

[2] A. M. Vasilev, "Trans. Commission on Analytical Chemistry" Vol 1 (IV), 28 (1947)

[3] I. M. Korenman, "Organic Compounds in Factory Air" 245, ONTI Chem. Theoret. (1935)

[4] V. I. Kuznetsov, Factory Labs. 9, 768 (1945)

[5] L. G. Makarova and A. N. Nesmeyanov, "Synthetic Methods in the Field of Metallorganic Mercury Compounds. Published by the Acad. Sci. of the USSR, 43-48 (1945)



Received April 4, 1950

# THE ANALYTICAL USE OF POTASSIUM MANGANATE HYDROLYSIS

S. F. Zavgorodny

Quantitative determination of manganate and permanganate when they occur simultaneously is based on the oxidation-reduction process

$$3MnO_4^{2-} + 2H_2O \rightarrow MnO_2 + 4OH^- + 2MnO_4^- , \quad (1)$$

which is sometimes called the manganate hydrolysis. Walde and Schuh [1] first proposed that this reaction could be used for analytical purposes. For this end the test solution is treated with $CO_2$ until $MnO_2$ ceases to be formed, when it is dissolved in sulfurous acid ($SO_2 + H_2O$) and the $Mn^{2+}$ determined by the pyrophosphate method.

It has been postulated that the reaction proceeds as follows -

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + MnO_2 + 2KMnO_4. \quad (2)$$

Total manganate and permanganate are first determined in another aliquot by the oxalate method. Sokolova [2] decomposed the manganate with potassium bisulfate

$$3K_2MnO_4 + 4KHSO_4 = 2KMnO_4 + MnO_2 + 4K_2SO_4 + 2H_2O. \quad (3)$$

When the $MnO_2$ has been filtered off, the permanganate in solution is then also determined by the oxalate method. According to Centnerszwer [3] who checked the $CO_2$ method, reaction (2) only proceeds when there is five times more permanganate than manganate, if there is no excess the error in determination can be as much as 50 %. This author concluded that in the absence of permanganate or when only a small amount of it is present in solution, the decomposition of manganate by $CO_2$, or by acids is accompanied by formation of oxide and not dioxide of manganese.

$$6K_2MnO_4 + 4CO_2 = 4KMnO_4 + 4K_2CO_3 + Mn_2O_3 + O. \quad (4)$$

Centnerszwer proposed that the manganese be decomposed with $H_2SO_4$ or $HNO_3$ (10-15%) and depending on the permanganate content of the solution, calculate the analytical results according to (2) or (4). The necessity of using two equations for calculating the results is a real drawback of the method. Moreover the use of comparatively concentrated solutions 0.2 M $KMnO_4$ and 0.5 M $H_2C_2O_4$ – must also lead to an additional error which is considerable.

In order to find out what are the optimum conditions for the analytical application of the manganate hydrolysis [1] the author of the present article experimentally verified the $CO_2$, bisulfate, and $HNO_3$ - $H_2SO_4$ method. The manganate used for analysis was prepared by boiling 0.2 M $KMnO_4$ with 50% KOH. The test mixtures were prepared before each determination by pouring into a 250 ml standard flask measured amounts of $K_2MnO_4$ and $KMnO_4$ solutions respectively and the solutions made up to standard volume with a 2-3 N KOH. The original solutions contained 0.00547 g $K_2MnO_4$ and 0.04914 g $KMnO_4$.

The procedure adopted was as follows: 50 ml of the manganate-permanganate mixture was treated with the respective reagent to decompose the manganate. The solution was then filtered free from $MnO_2$ by means of a No. 3 sintered glass filter the precipitate was washed free of permanganate with warm water and dissolved in 0.1 N $H_2C_2O_4$ containing $H_2SO_4$ by warming. Excess oxalic acid was determined by means of permanganate. The filtrate containing the permanganate in solution ("both the original permanganate-"primary", - and that formed during the reaction –"secondary"") was transferred to a 250 ml standard flask and made up to the mark with water. This permanganate was also determined by the oxalate method using 50 ml aliquots. The analytical results were calculated as follows. From 1 it follows that the 12 oxygen equivalents of 3 mols of manganate correspond to the 2 oxygen equivalents of the 2 mols of $MnO_2$. Consequently, by multiplying the number of mols of $H_2C_2O_4$ (0.1N) used for the determination of $MnO_2$ by 6, and the titer for 0.1 N $K_2MnO_4$ by 0.004928 we can find the amount of manganate in the aliquot taken. In order to determine the amount of permanganate formed during the reaction, the value found for the manganate content is divided by 1.871. This coefficient is determined from the ratio:

$$\frac{3K_2MnO_4}{2KMnO_4} = \frac{3 \cdot 197.13}{2 \cdot 158.03} = 1.371$$

The permanganate originally in solution before reaction is determined by subtracting the amount of permanganate formed during the reaction from the total amount of permanganate contained in the filtrate. From the results obtained, which are given in Table 1, it is clear that satisfactory results are obtained only when the solution contains not less than 10 mols of permanganate/mol of manganate and not 5 times as Centnerszwer indicated.

TABLE 1

| No. | Amount taken | | Molar ratio | Amount found | | | | Method used |
|---|---|---|---|---|---|---|---|---|
| | $K_2MnO_4$ in g | $KMnO_4$ in g | $\frac{KMnO_4}{K_2MnO_4}$ | $K_2MnO_4$ | | $KMnO_4$ | | |
| | | | | in g | % error | in g | % error | |
| 1 | 0.0492 | 0.1368 | 3.45 | 0.0377 | 23.40 | 0.1270 | 7.15 | $CO_2$ |
| 2 | 0.0492 | 0.1999 | 5.07 | 0.0457 | 7.15 | 0.1964 | 1.73 | $CO_2$ |
| 3 | 0.0492 | 0.3684 | 9.34 | 0.0483 | 1.75 | 0.3654 | 0.81 | $CO_2$ |
| 4 | 0.0492 | 0.4402 | 11.15 | 0.0489 | 0.53 | 0.4385 | 0.38 | $CO_2$ |
| 5 | 0.0428 | 0.1082 | 3.16 | 0.0328 | 23.18 | 0.0993 | 8.24 | bisulfate |
| 6 | 0.0428 | 0.2576 | 7.46 | 0.0412 | 3.69 | 0.2487 | 3.43 | bisulfate |
| 7 | 0.0428 | 0.3284 | 9.60 | 0.0423 | 1.02 | 0.3231 | 1.61 | bisulfate |
| 8 | 0.0428 | 0.4402 | 12.84 | 0.0425 | 0.42 | 0.4364 | 0.87 | bisulfate |
| 9 | 0.0369 | 0.1190 | 4.01 | 0.0343 | 7.06 | 0.1119 | 5.92 | $HNO_3+H_2SO_4$ |
| 10 | 0.0369 | 0.1694 | 5.73 | 0.0354 | 4.12 | 0.1623 | 4.08 | $HNO_3+H_2SO_4$ |
| 11 | 0.0369 | 0.2240 | 7.58 | 0.0359 | 2.71 | 0.2198 | 1.88 | $HNO_3+H_2SO_4$ |
| 12 | 0.0369 | 0.2971 | 10.01 | 0.0367 | 0.43 | 0.2961 | 0.34 | $HNO_3+H_2SO_4$ |

The use of only equation (3) for calculation of the analytical results did not give satisfactory results; the mean error amounted to 10-15%. By analysis of solutions of manganate not containing permanganate it was shown that in this case the amount of $KMnO_4$ and $MnO_2$ formed agreed with the values calculated theoretically from equation(1). Thus when 0.1924 g $K_2MnO_4$ (40 ml) was decomposed with $H_2SO_4$ 0.0284 g $MnO_2$ and 0.1037 g $KMnO_4$ were obtained the theoretical values were 0.0286 and 0.1041 g, respectively.

These experiments showed that Centnerszwer was wrong about the above mentioned scheme. Apparently, the source of error, during analysis of solutions where the molar ratio of permanganate to manganate is less than 10, is the formation of precipitates, the compositions of which vary between $Mn_2O_3$ and $MnO_2$. Mendeleev [4] cited the action of $Na_2SO_3$ on permanganate, forming a colloidal precipitate $Mn_2O_3 \cdot 4(MnC_2 \cdot H_2O)$. Dubois [5] indicates that a series of oxides containing $MnO_2$ as one of the components can exist in the range $Mn_2O_3$ and $MnO_2$. Thus, $MnO_{1.93} = Mn_{15}O_{31} = 15MnO_2 \cdot MnO$ can occur. $MnO_2$ present in a colloidal form might also affect the accuracy of the determination of $KMnO_4$ because it adsorbs manganate in preference to permanganate. If the existence of the higher oxides indicated above is accepted as being probable, then the preferential adsorption of $K_2MnO_4$ can be explained in accordance with the Fajans-Hahn rule, by the formation of insoluble manganese manganate.

When there is a considerable excess of $KMnO_4$, apparently the relative amount of $K_2MnO_4$ adsorbed by the precipitate decreases. In order to confirm the relation obtained above, a method of additions was adopted in which a known amount of permanganate solution of known strength* was added before carrying out the decomposition of $KMnO_4$. The amount of permanganate to be added was determined from the color of the test solution. Requisite amounts of permanganate, indicated in Table 2, were added to solutions of the same concentrations as given in Table 1, in which the molar ratio of permanganate to manganate was less than 10. The results obtained were completely satisfactory.

Thus, by adding the necessary amount of permanganate to the test solution, it is possible to analyze solutions containing any ratio of the components. An analysis takes half an hour.

*This was also successfully applied in the ferrocyanide method of analyzing solutions of manganates and permanganates when both were present simultaneously. [6]

TABLE 2

| No. | $KMnO_4$ added in g | New ratio (molar) $\frac{KMnO_4}{K_2MnO_4}$ | Found | | | | Method used |
|---|---|---|---|---|---|---|---|
| | | | $K_2MnO_4$ | | $KMnO_4$ | | |
| | | | in g | % error | in g | % error | |
| 1 | 0.3322 | 11.88 | 0.0490 | −0.44 | 0.1363 | −0.41 | $CO_2$ |
| 2 | 0.3322 | 13.50 | 0.0494 | +0.36 | 0.1994 | −0.24 | $CO_2$ |
| 3 | 0.3422 | 13.95 | 0.0429 | −0.40 | 0.1079 | −0.29 | bisulfate |
| 4 | 0.4224 | 19.80 | 0.0427 | −0.27 | 0.2582 | +0.24 | bisulfate |
| 5 | 0.3084 | 14.44 | 0.0368 | −0.27 | 0.1192 | +0.22 | $HNO_3 + H_2SO_4$ |
| 6 | 0.3282 | 16.45 | 0.0370 | +0.32 | 0.1689 | −0.30 | $HNO_3 + H_2SO_4$ |

## SUMMARY

1. Methods for the analysis of manganate-permanganate solutions which are based on hydrolysis of the manganate have been checked and the limits of their application indicated. The correctness of the generally accepted scheme for manganate hydrolysis was confirmed.

2. It is postulated that the error in the determination of manganate in cases where there is a relatively low concentration of permanganate can be explained by formation of oxides intermediate between $Mn_2O_3$ and $MnO_2$, and partial adsorption of manganate by colloidal $MnO_2$.

3. It has been shown that preliminary addition of known amounts of permanganate to test solutions enables solutions containing any ratio of the components to be analyzed fairly accurately.

## LITERATURE CITED

[1] H. Walde and K. Schuh, Wissenshaftliche Veroffentlichungen aus Siemens-Konzern, 4, 2, 188 (1925)

[2] L. N. Sokolova. Factory Labs. 3, 9, 805 (1934)

[3] M. Centnerszwer, Bull. Soc. Chem. 5,5,10, 1531 (1938)

[4] D. I. Mendeleev, "Fundamentals of Chemistry" 2, 462 (1932)

[5] P. Dubois, Ann. Chem. II Serie, 5, 411 (1936)

[6] S. F. Zavgorodny, Trans. Commission on Anal. Chem. VI, 282 (1951)

Received June 5, 1950

# A COMPARATIVE EVALUATION OF QUALITATIVE REACTIONS FOR BISMUTH CARRIED OUT BY TRITURATION

E. P. Ozhigov•

Far East Branch of the USSR Academy of Sciences

As Flavitsky [1,2], and, in recent years, a number of Soviet research workers [3-9], have shown, qualitative chemical analysis involving the use of trituration methods enable the majority of elements of practical importance to be determined in their salts, minerals, and certain ores. The speed with which the method can be carried out and the extreme simplicity of the apparatus make these methods ideal ones for geological parties under field conditions [5,9]. This method, however, has not been tested very much on ores of various types, and the sensitivity and specificity of the individual reactions have not been established as clearly as they should have. Thus, Isakov [3,5] gives four examples of qualitative reactions for bismuth in which various reagents were used [ammonium thiocyanate, pyrogallol, sodium thiosulfate, and ammonium hexathiocyanate chromite $(NH_4)_3\,Cr(CNS)_6$] without any comparative evaluation of the different reactions.

Reactions with sodium thiosulfate are not specific for bismuth. Thus, silver, which is often present in lead ores in addition to bismuth, gives a similar color. The reaction of bismuth with ammonium thiocyanate is not specific in the presence of iron because of the necessity of reducing trivalent iron with thiosulfate. The fact that these individual questions have not been dealt with fully enough hinders the wide use of the method and its adoption for field testing.

The aim of the present paper is to check the application of qualitative reagents for bismuth which are carried out by trituration on samples of galenite and other ores of a definite type, and to work out the conditions for which the reaction will be most sensitive and selective.

The ore tested was a typical polymetallic ore and in addition to bismuth contained lead, zinc, copper, antimony, arsenic, sulfur, manganese, silver, magnesium, iron, aluminum and other elements. Some samples contained considerable amounts of iron.

In all the tests, bismuth was determined colorimetrically using thiourea, while in the samples of galenite containing bismuth it was determined spectrographically.

Preliminary experiments showed that $H_2SO_4$ does not ensure complete decomposition of the material with the formation of white colored salts. Decomposition of galenite by $H_2SO_4$ was particularly unsatisfactory, even after two treatments it remained undecomposed and had a grey color. The test materials were accordingly decomposed by successive treatment with $HNO_3$ and $H_2SO_4$.

Table 1 shows the advantages of treating galenite with the two acids. The sensitivity of the bismuth determination is increased. In the presence of bismuth, the color of the reaction product after trituration with $Na_2S_2O_3$, which depends on the bismuth content, varies from blood-red or brown to a weak yellow or lemon.

Four qualitative reactions for bismuth were experimentally tested with: pyrogallol, ammonium thiocyanate, sodium thiosulfate and ammonium hexathiocyanatochromite.

## a) Reactions with Pyrogallol

0.03 g galenite was treated in a porcelain beaker with the acids and after evaporation to dryness the residue was triturated with 3-4 crystals of pyrogallol. According to Isakov the reaction products should be colored pale green. In the test samples of galenite and the other ores the color of the reaction products varied from a pale violet to a dark violet and only on wetting with water did the change to green occur and that only in some instances. In the majority of cases, wetting the product with water led to blackening.

• V. L. Alpatova participated in the experimental work.

TABLE 1

| Bismuth content of the test samples | | Color of the reaction product with $Na_2S_2O_5$ after decomposition of galenite | |
|---|---|---|---|
| in fraction of a % | in % | with $H_2SO_4$ | with $HNO_3$ and $H_2SO_4$ |
| units | 3.2; 1.24; 1.21 | from blood-red to dirty-grey | from brown to blood-red |
| tenths | 0.86 | weak red | blood-red of lesser intensity |
| hundredths | 0.07 | bismuth not detected | pale-lemon |

Reactions with pyrogallol are therefore unsuitable for qualitative determinations of bismuth in galenite and in the other types of ore tested.

b) Reactions with Ammonium Thiocyanate

In the presence of trivalent iron the mixtures were colored reddish-brown. Isakov recommended that during triturations a small amount of crystalline $Na_2S_2O_3 \cdot 3H_2O$ be added to the ammonium thiocyanate in order to reduce the trivalent iron, when this was done the reddish-brown color disappears while the yellow color of ammonium thiocyanate appears. Since thiosulfate acts as a reagent for silver we used another reducing agent for iron – $Na_2SO_3$ – which does not give a color with bismuth, silver, or the other elements.

TABLE 2

| Bismuth content of the test samples | | | Color after trituration with | | |
|---|---|---|---|---|---|
| in fractions of a % | in % | in μg | $NH_4CNS$ | $Na_2S_2O_5$ | $(NH_4)_3[Cr(CNS)_6]$ |
| units | in galenite 3.2;1.24, 1.12 | 960,373,336 | intense orange | blood-red | orange-red, sometimes with grey shades. |
| tenths | in galenite 0.86 | 258 | orange | from blood-red, less intense to grey-yellow | from orange-red, less intense, to light-green shades. |
| hundredths | in galenite 0.011, 0.071 | 3.3; 21 | weak orange to canary-yellow | light lemon sometimes with dirty-grey shades | weak orange-red, sometimes with violet and green shades. |
| | in ore 0.014,0.038 | 4.2; 11.4 | | | |
| thousandths | in the ore 0.005; 0.008 0.008 | 1.5; 2.4;1.4 | yellow | grey-yellow sometimes with greenish shades. | weak orange-red, less intense. |

Reactions with ammonium thiocyanate in the presence of sodium sulfite are characterized by fair sensitivity and specificity (Table 2). By this method 0.00136 mg or 1.37 μg can be detected in 0.03 g of test material.

c) Reactions with Sodium Thiosulfate

The test powder of mineral or ore after treatment with $HNO_3$ and $H_2SO_4$ and evaporation was triturated with 1-2 crystals of sodium thiosulfate $Na_2S_2O_3 \cdot 3H_2O$. No appreciable color was observable immediately after doing this, but gradually, on standing in the air, a pale yellow color appeared which quickly changed into a stable blood-red color. Table 2 shows that these reactions with sodium thiosulfate are not so sensitive as the reactions with ammonium thiocyanate.

Using this reaction 0.00274 mg or 2.74 μg of bismuth can be detected in a sample.

d) Reactions with Ammonium Hexathiocyanatochromite

The powdered mineral or ore after treatment with the acids was triturated with 1-2 crystals of ammonium hexathiocyanatochromite. In the presence of bismuth a red-orange color develops because of the formation of $Bi[Cr(CNS)_6]$

$$Bi_2(SO_4)_3 + 2(NH_4)_3[Cr(CNS)_6] = 2Bi[Cr(CNS)_6] + 3(NH_4)_2SO_4.$$

On checking this it was observed that the red-orange color can be masked by shades of different colors from violet to green. Because this change from one color to another is not very clear cut, the reaction is less sensitive than the reactions with ammonium thiocyanate and sodium thiosulfate.

A comparison of the results obtained by the last three methods is given in Table 2.

The reaction with ammonium thiocyanate can be used as a semiquantitative method for the detection of bismuth in polymetallic ores and products obtained by treatment of these ores, since the color intensity (from orange to yellow) depends on the bismuth content of the aliquots, and is not masked by other colors.

## SUMMARY

1. Comparative tests have been made of qualitative reactions for bismuth using a trituration technique with pyrogallol, ammonium thiocyanate, sodium thiosulfate, and ammonium hexathiocyanatochromite.

2. It has been established that the most sensitive reaction for bismuth is the one with ammonium thiocyanate; the intensity of the yellow color produced is dependent on the bismuth content.

3. It is better to use sodium sulfite and not sodium thiosulfate (as recommended by Isakov) for the reduction of trivalent iron when using ammonium thiocyanate for the detection of bismuth.

## LITERATURE CITED

[1] F.M. Flavitsky, J. Russ. Chem. Soc. 30, 216 (1896).

[2] F.M. Flavitsky, Original Equations in Analytical Chemistry, 1907.

[3] P.M. Isakov, Scientific Bulletin of the Leningrad State University, P.T.O. No. 21, 1948; No. 25, 1950; No. 27, No. 28, No. 29, 1951; No. 30, 1952.

[4] P.M. Isakov, Field Qualitative Chemical Analysis of Ores and Minerals, State Geol. Press, 1950.

[5] P.M. Isakov, J. Anal. Chem. 6, 65 (1951).

[6] A. Kh. Batalin, E. Yu. Perelman, Communications on the Scientific Work of Members of the All-Union Chemical Society, Vol. 2, 1950.

[7] N. A. Khmelevskaya, Proc. Mendeleev Chem. Soc. (Chkalov Section), No. 4, 1951.

[8] L.V. Sadovskaya, Proc. Mendeleev Chem. Soc. (Chkalov Section), No. 4, 1951.

[*]

Received September 5, 1952

---

• Although there is a literature reference [9] in the original Russian paper, no [9] appears in the Russian literature citations. Publisher.

# DETERMINATION OF VAPORS OF FLUOORGANIC COMPOUNDS IN AIR

E. A. Peregud and R. S. Rotkina
State Scientific-Research Institute for Industrial Hygiene and Occupational Hazards, Leningrad.

Analysis of small amounts of highly volatile and gaseous fluoorganic compounds presents considerable difficulty.

The special characteristics of fluoorganic compounds necessitate special techniques for their analysis, and several of the conventional methods used for analysis of other halo-organic compounds are not applicable.

Thus, determinations by means of the lamp method which we have used for the analysis of a number of halogen compounds are out of the question, because the surface of the lamp glass is attacked by HF formed during combustion. Decomposition of fluoorganic compounds by alkali metals is impracticable because of the effect of the salts formed on neutralization on the subsequent determination of the fluorine ion. The normal method of thermal decomposition in a calcined porcelain tube is also excluded because HF reacts with the inner walls of the tube.

Analysis of micro-amounts of fluoorganic compounds is complicated further by the absence of sufficiently sensitive methods for determination of fluorine ions.

The most expedient method for determination of small amounts of elements by chemical means is the colorimetric method. Fluorine ions, however do not give colored compounds, and the usual colorimetric method for fluorine is based on measuring the degree by which the color of various metal complexes is weakened on interaction with fluorine [1-9]. Naturally, methods based on this principle are not adequately accurate or sensitive, since measurements of the small extent of weakening of a color on an intensely colored background are extremely difficult.

Further, the known reactions of fluorine with colored complexes are themselves extremely variable with respect to pH and to the salt composition of the test solution.

All these drawbacks led us to seek for new methods of analyzing low concentrations of fluoorganic vapors.

During our investigations which were directed at working out a sensitive and accurate method, we settled on the principle of combustion of the vapors in a quartz tube with subsequent determination of the $SiF_4$ formed. In using this technique, it seemed interesting for the reasons adduced above, to estimate $SiF_4$ by its silicon and not its fluorine content. Such an approach was justified because we already had an accurate method for determination of silicon, and preliminary results on the possible diffusion of "volatile silicon" from the heated quartz tube were favorable.

After testing some volatile fluoorganic compounds we became convinced that we had hit on the right method.

Tests were carried out in an apparatus consisting of a tubular oven for high temperature decomposition, a transparent quartz tube of 6 mm diameter and 0.5 meter length, and micro-absorption bubblers of the Polezhaev type [see diagram]. $SiF_4$ was absorbed with distilled water.

Procedure. An aliquot of the fluoorganic compound in a small tube was cooled in ice and connected to the quartz tube, two micro-absorbers, each of which had been filled with 5 ml distilled water, were connected to the other end of the tube. When the temperature of the oven had reached 900°, the tap on the tube connecting the fluoorganic compound was opened, and the vapors distilled slowly through the system by means of an aspirator which could draw air through at the rate of 2 liters per hour. When 2 liters of air + vapor had been passed through the apparatus, the absorbers were replaced by new ones and 2 liters of pure air swept through. While this was being done, the cold end of the quartz tube was placed as near as possible to the combustion zone, in order to ensure complete vaporization of adsorbed $SiF_4$.

Silicon was then determined in the absorption solution by the color formed on formation of the blue silico-molybdate complex. The solution from each absorber was separately transferred to a flask of molybdenum

glass and diluted with water in accordance with concentration determined on a scale. To each 4 ml of test solution measured out into the colorimeter tubes, 1 drop of 0.1 N $H_2SO_4$, and 0.1 ml of ammonium molybdate* were added, and after shaking allowed to stand for 5 minutes for the color of yellow silicon molybdate complex to develop. At the end of this period 1 ml of 5% tartaric acid and 0.1 ml of freshly prepared 1% ascorbic acid solution were added. After 20 minutes, the intensity of the blue color was measured by comparison with a set of standards containing various amounts of chemically pure sodium silicate treated as described above.

The $Na_2SiO_3$ solution which was used for preparing the standard series contained 0.02 mg $SiO_2$/ml.

The series of standards used are given in Table 1.

Results of the tests on the weights given below of volatile fluoorganic compounds are given in Table 2.

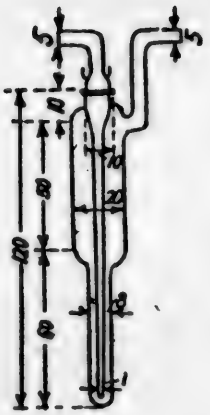


TABLE 1

| Standard solution (ml) | Corresponding amount of Si (mg) | Distilled water (ml) |
|---|---|---|
| 0 | 0 | 4.0 |
| 0.06 | 0.0006 | 3.94 |
| 0.13 | 0.0012 | 3.87 |
| 0.25 | 0.0023 | 3.75 |
| 0.38 | 0.0035 | 3.62 |
| 0.50 | 0.0047 | 3.50 |
| 0.63 | 0.0059 | 3.37 |
| 0.75 | 0.0070 | 3.25 |
| 0.88 | 0.0082 | 3.12 |
| 1.00 | 0.0093 | 3.00 |

TABLE 2

| Amount taken (mg) | Amount found (mg) | Amount found (%) |
|---|---|---|
| 6.6 | 6.70 | 101.5 |
| 7.8 | 7.65 | 98.0 |
| 8.0 | 7.60 | 95.0 |
| 8.0 | 7.65 | 95.6 |

In order to simulate the actual problem—determination of small amounts of fluoorganic vapors in air—the experimental conditions were modified to carry out measurements on given concentrations of the vapor in the gaseous phase.

A drop of liquid, the weight of which had been previously determined, was introduced into a 9-liter flask fitted with a ground glass stopper with two tubes—a short and a long one. The taps on the outlet tube were closed and by slight heating the substance was vaporized. The 9-liter flask was then connected to an apparatus whereby the mixture of air plus vapor could be expelled from it. This was achieved by passing a saturated solution of NaCl into the flask. NaCl solution was fed in by a siphon from a measuring cylinder.

All the other experimental conditions, combustion of test material in quartz tube, absorption of $SiF_4$ and subsequent determination of Si, were the same as in the first series.

By conducting the tests in this way it was possible to measure out very small amounts of substance into the gaseous phase and to study the best methods for testing and subsequent treatments of test samples.

TABLE 3

| Air drawn through in ml | Amount of test material in mg | Amount determined in mg |
|---|---|---|
| 500 | 0.80 | 0.86 |
| 300 | 0.48 | 0.48 |
| 100 | 0.16 | 0.153 |
| 100 | 0.16 | 0.153 |
| 50 | 0.08 | 0.076 |
| 500 | 0.457 | 0.57 |
| 500 | 0.457 | 0.428 |
| 300 | 0.274 | 0.23 |
| 150 | 0.137 | 0.135 |
| 150 | 0.137 | 0.160 |
| 100 | 0.0915 | 0.084 |
| 100 | 0.0915 | 0.088 |

TABLE 4

| Substance in mg | |
|---|---|
| Passage through 5% NaOH | Without alkali |
| 0.80 | 0.765 |
| 0.335 | 0.325 |
| 0.450 | 0.428 |
| 0.153 | 0.153 |
| 0.084 | 0.088 |
| 0.076 | 0.076 |
| 0.069 | 0.068 |
| 0.069 | 0.065 |

The results of Table 3 show the agreement between amount of sample taken and amount actually determined, and also the reproducibility of the results.

Since it is possible that HF may be present in the air as well as the vapors of volatile fluoorganic compounds

* 18.8 g of chemically pure ammonium molybdate was measured into a 250 ml flask, dissolved in water, and 80 ml of 10 N $H_2SO_4$ added and the volume made up to the mark.

we carried out an independent series of determinations in which the gas-air mixture entering the oven was first sucked through 5% NaOH. Parallel experiments in which the air-vapor mixture was not scrubbed with 5% NaOH but in which all other conditions were identical showed that dilute NaOH is quite a suitable absorbent for HF as Table 4 shows.

## SUMMARY

A method has been worked out for the determination of vapors of fluoorganic compounds in air. It is based on the combustion of the substance in a quartz tube at 900°; the $SiF_4$ formed is absorbed in water and is determined colorimetrically via silicon by means of the silico-molybdate complex. The air is removed into an evacuated gas pipet or bottle and forced into the combustion apparatus by means of saturated NaCl solution.

If HF is present in addition to fluoorganic compounds, the vapor-air mixture is passed through gas scrubbers filled with dilute NaOH before going on to the combustion furnace.

This scheme of analysis for volatile and gaseous fluoorganic compounds should be capable of application to a number of cases.

Because of the large variety of fluoorganic compoundsand their individual characteristics, however, it would be better to carry out an experimental check on each one individually, using concentrated material.

## LITERATURE CITED

[1] L.S. Chemodanova, Factory Labs. 12 (1937).

[2] Raines and Kazachkova, J. App. Chem. I (1940).

[3] A.K. Babko, Factory Labs. XIII, 7, 803 (1947).

[4] A. A. Vasilev, Factory Labs. XIII, 7, 797 (1947).

[5] L.M. Dubinkov and I.F. Tikhomirov, Factory Labs. XIII, 7, 773 (1947).

[6] N.S. Nikolaev, Factory Labs. XIII, 807 (1947).

[7] M.A. Feldman, Scientific Proc. of Dnepropetrovsk University. XXXIII, 47 (1948).

[8] M.A. Portnov and S.I. Elkina, Factory Labs. XIII, 7, 822, (1947).

[9] T.S. Luzina, Factory Labs. XV, 12, 1412 (1949).

[10] Huckabay, Busey and Metler, Anal. Chem. 19, A, 59-63 (1947).

[11] Miller, Hunt and McRee, Anal. Chem. 19, No. 1, 148 (1947).

[12] Miller, Hunt, Hass and McRee, Anal. Chem. 19, No. 1, 148 (1947).

[13] Kimball and Tufts, Anal. Chem. 19, XI, 150 (1947).

[14] Nichols and Olsen, Ind. and Eng. Chem., An. Ed. 5, 342 (1943).

[15] H. Hill and C. Reynolds, Anal. Chem. 3, 448 (1950).

[16] D. Monnier, R. Vaucher, P. Wenger, Helv. Chim. Acta. 33, No. 1, 1 (1950).

[17] O. Milner, Anal. Chem. 22, No. 2, 315-317 (1950).

[18] H. Clark, Anal. Chem. 23, No. 4, 659 (1951).

[19] M. Gilbert and Saylor, Anal. Chem. 22, No. 1, 196 (1950).

Received December 31, 1951

# p-ANISIDINE – A SENSITIVE REAGENT FOR CUPRIC CATIONS

A. Kh. Batalin

p-Anisidine or the methyl ether of p-aminophenol $H_2NC_6H_4OCH_3$ is a solid which melts at 57° and boils at 240°. It dissolves readily in organic solvents, but is not so soluble in water. Aqueous solutions are the most stable. Solutions of p-anisidine in organic solvents rapidly turn brown in the air, aqueous solutions can be stored without any significant change (in dark bottles) for 3-5 months. Aqueous solutions were used in most of the experiments described below.

p-Anisidine, like other amines, gives a number of characteristic changes on reaction with cupric cations. Experiments have shown that the character of this reaction changes in the presence of alkali metal halides and thiocyanates. Accordingly, mixtures of the reagent with these compounds were also tested.

The reagent was prepared by adding 1 ml of a saturated solution of p-anisidine in water to 10 ml of water. The reagent in admixture with halides or thiocyanates ("thiocyanate", or "iodide", or "bromide" reagents) was prepared by adding 1 ml of a saturated solution of p-anisidine in water to 100 ml of 0.1 N halide or thiocyanate. 2-3 drops of reagent solution are sufficient to give the corresponding reactions with 1 ml of 0.1 N solution of $Cu^{2+}$.

When aqueous solutions of p-anisidine react with $Cu^{2+}$ cations, a yellow-green precipitate is initially formed, which rapidly turns brown and, after 5-8 minutes, acquires a dark-violet color. Solutions of low concentration of $Cu^{2+}$ are colored a violet color, on addition of reagent no precipitate is formed. The yellow-green precipitate formed on addition of a drop of mineral acid also acquires a brown color. The sensitivity of the p-anisidine–$Cu^{2+}$ reaction is fairly high – about 4 μg in 1 ml. Iron, silver, mercury, and oxidizing anions interfere.

The reaction is different when "thiocyanate" or "iodide" reagents are used; in such cases, dark red precipitates are formed when the cupric solution is concentrated while the solution becomes a cherry color when the cupric concentration is low. The precipitates (or solutions) obtained keep their color for 10-15 hours, and hardly change at all when heated to 100°. The color of the precipitates or solutions is removed on addition of ammonia, citrates, pyrophosphates and addition of a large excess of mineral acid. The sensitivity of the "iodide" or "thiocyanate" reagents for cupric ions is very high-ca 0 6 μg/ml so that the limiting dilution is 1 600,000.

It is of interest to note that the "chloride" reagent only gives an effect when there is a large excess of chloride present. The "bromide" reagent gives a fairly definite reaction, but this must also be done in the presence of a large excess of bromide

Experiments have shown that the sensitivity of the reaction for cupric ions is not diminished even in the presence of a 500-fold amount of Mn, Al, Zn, Mg, Ni, Cr, alkaline metals, alkaline-earth metals, and $Fe^{2+}$; a 50-fold amount of Co, Ag, Sn, uranyl, Ce, $Hg^{2+}$, Pb, and 5-fold amounts of Sb and Hg. Greater amounts of indifferent ions lead to a sharp reduction in the reaction sensitivity.

For qualitative detection of $Cu^{2+}$ in the presence of $Fe^{3+}$ and in the absence of oxidizing agents the masking action of NaF is used. To the test solution is added a saturated solution of NaF and a few drops of a "thiocyanate" reagent. In the presence of cupric ions the solution acquires a red-violet color, or if large amounts of cupric ions are present, a dark red precipitate is formed. The reactions are best carried out in a neutral or weakly acid medium pH 6.8-6.9.

Received October 14, 1951

# DETERMINATION OF INDICATOR ERROR BY THE KORENMAN METHOD FROM THE WEIGHT OF SUBSTANCE

I. L. Teodorovich

[The V.M. Molotov Tashkent Medical Institute]

In the determination of the indicator error by Korenman's method* two volumes of the solution to be titrated are measured out, one of which should be twice or (n)** times the other [where n is a whole number].

When a dry substance is used it is practically impossible to weigh two aliquots on a micro-balance so that one is an exact number of times more than the other. We therefore took two weights $m_1$ and $m_2$ such that $m_2 \approx 2m_1$ and dissolved them in known volumes of water, an equal amount of indicator was then added to each

$m_2$ was titrated first, water was then added to $m_1$ so that at the end of titration the volume of liquid in both vessels was approximately equal.

If $a$ is the amount in mg-equivalents in $m_1$, $\Delta a$ and $\Delta$ the indicator error expressed in mg-equivalents and ml respectively, $b = m_2/m_1$, and $v_1$ and $v_2$ the volumes of solution with normality $Nx$ in mg-equivalents/ml used for titrating $m_1$ and $m_2$ respectively, then

$$a + \Delta a = v_1 Nx. \qquad (1)$$

$$b\,a + \Delta a = v_2 Nx. \qquad (2)$$

Multiplying (1) by $b$, determining $\Delta a$ from (1) and (2) and dividing by $Nx$ we get

$$\Delta = \frac{bv_1 - v_2}{b-1} \text{ ml}. \qquad (3)$$

I.M. Korenman's formula is written in a similar form suitable for calculation. Results determined by formula (3) are adduced below.

Determination of the Normality of NaOH Solution by Titration with Potassium bi-iodate.

| Normality of NaOH solution | Weight of $KH(IO_3)_2$ | $b = \frac{m_2}{m_1}$ | Indicator | NaOH used in ml | Indicator error in ml NaOH | Corrected volume of NaOH in ml | Normality calculated for NaOH solution |
|---|---|---|---|---|---|---|---|
| 0.0100 | 4.481 | – | Methyl | 1.20 | +0.07* | 1.13 | 0.01017 |
| 0.0100 | 10.816 | 2.414 | red | 2.80 | | 2.73 | 0.01016 |
| 0.0200 | 5.160 | – | Phenol- | 0.75 | +0.08* | 0.67 | 0.01975 |
| 0.0200 | 9.398 | 1.821 | phthalein | 1.30 | | 1.22 | 0.01976 |

* The positive errors in both examples are explained by a special case of formation of complex bi-iodate aquo-acids

Received April 18, 1951

* I. M. Korenman, Factory Labs. 1, 32, (1936).

** I.M. Korenman did not point out that n is a whole number. In all the examples given however n was equal to two.

## CRITICISM

### Reply to A. K. Babko's Criticisms of the Article, "The Quantitative Determination of Trivalent Iron with Tetraborate" (J. Anal. Chem. 7, 280 (1952)

Since our work is of an original nature and includes a new direct method for the determination of $Fe^{3+}$, in which it was postulated that new, complex iron compounds were formed, we are glad of the opportunity to discuss the problem and are accordingly grateful for the chance to reply to criticisms of this question.

Babko's criticisms, however, are not a valuable contribution to the discussion, particularly in view of his far-from-scientific way of putting forward his views. In turning to the basis of the criticisms made, we, on our part, have the following to say.

First of all, Babko's fundamental observation that the electrode which we used was the wrong one, in connection with which he reproached us for "disregarding the fundamental theoretical postulates of the theory of potentiometric titration", is inappropriate for the following reasons.

Babko suggests that we should have used as standard electrode an electrode whose potential depends ina definite way on the concentration of one of the reacting ions, in particular the Pt electrode in the system $Fe^{2+} - Fe^{3+}$. This electrode, however, as well as a number of others (including the quinhydrone and the iron electrode) were studied by us in detail before we decided to use the Pt/Pt-black electrode for the potentiometric titration of $Fe^{3+}$ with borate. According to our results, both Pt electrodes gave similar results for the titration but since the smooth Pt electrode required 5-10 minutes for the potential to be established, while the Pt/Pt-black electrode took only one minute and seemed to be more sensitive, we decided to use the latter. The behavior of the Pt electrodes in our system can be represented as follows: a solution of an $Fe^{3+}$ salt always contains traces of $Fe^{2+}$, i.e., solutions of $Fe^{3+}$ salts are oxidation-reduction systems. The measurement of the potential of Pt electrodes in solutions of $Fe^{3+}$ salts during their potentiometric titration with borate is determined on the one hand by a decrease in the concentration of $Fe^{3+}$ ions during the process in which they are gradually linked up into fairly stable complex compounds, and on the other hand by oxidation of $Fe^{2+}$ by aerial oxygen adsorbed by the platinum. The excess of borate added after the equivalence point creates an alkaline medium so that when the $Fe(OH)_2$ takes the adsorbed oxygen from the platinum electrodes to form $Fe(OH)_3$ a sharp potential jump occurs. A completely analogous picture has been observed on a smooth Pt electrode in the system $Ag^{+}-Ag_2^{2+}$. In order to show that the concentration of $Fe^{2+}$ in the solution actually affects the electrode potential, we potentiometrically titrated $Fe^{3+}$ with borate in the presence of various amounts of $Fe^{2+}$, and also measured the potentials of the Pt electrodes on addition of increasing amount $Fe^{2+}$ to them.

An increase in $Fe^{2+}$ concentration leads to a large decrease in electrode potential.

Babko's main objection is therefore removed.

With regard to Babko's other criticisms we say that some of his assertions contradict facts that are well known in chemical literature.

Thus, Babko affirms that excess of a coordinating ion leads to formation of more stable complex compounds, while our results agree completely with the conclusion of A. K. Babko and coworkers who determined the instability constants of a number of complex iron compounds, from which it was obvious that with increasing concentration of the coordinating ion the stability of the complex compounds decreased, e.g., in Babko and Kleiner's article,[••]

$$K_{[FeCNS]^{2+}} = 5\cdot10^{-3};\quad K_{[Fe(CNS)_2]^{+}} = 10^{-1.9};\quad K_{[Fe(CNS)_3]} = 10^{-1.4};$$

$$K_{[Fe(CNS)_4]^{-}} = 10^{0.8}$$

or in Babko's article:[•••]

$$K_{[FeSal]^{+}} = 4\cdot10^{-17};\quad K_{(FeSal_2]^{-}} = 4\cdot10^{-12};\quad K\,[FeSal_3]^{3-} = 2\cdot10^{-6}$$

---

• A. Obrucheva, J. Phys. Chem. 11, 473 (1938)

•• A. K. Babko, K. E. Kleiner, J. Anal. Chem. 1, 106 (1946)

••• A. K. Babko, J. Gen. Chem. 9-10, 745 (1945)

We got similar results:

$$K_{[FeB_4O_7]^+} = 1.78 \cdot 10^{-17}; \quad K_{[Fe_2(B_4O_7)_3]} = 0.7 \cdot 10^{-19}.$$

The appearance of a precipitate during titration of $Fe^{3+}$ with borax on addition of an excess drop of borax after the equivalence point is explained by the fact that $Fe^{3+}$ in solution $[Fe_2(B_4O_7)_3]$ is of the order of $10^{-5}$ g-ion/liter, i.e., is at a concentration far greater than the $[Fe^{3+}]$ essential for the precipitation of basic salts and $Fe(OH)_3$, i.e., of the order of $10^{-10}$ g-ion/liter.

Babko without any foundation asserts that we did not determine the pH of the solution. We did, however, carry out a series of pH determinations which we were unable to publish because of lack of space. In the present reply, however, we have adduced a curve showing pH changes during titration of $Fe^{3+}$ with borax.

Babko also pointed out that it is a serious drawback that we only gave values of $\Delta E/D\Delta$ instead of the values of the potential itself. Surely Babko must be aware that there are three graphical methods of presenting the results of potentiometric titrations which are of equal value: (1) E against V; (2) $\Delta E/\Delta C$ against C and finally, (3) $\Delta F/\Delta V$ against V. We chose (1) (which is not included in the published results) and (3). (3) has been used in a number of chemical investigations in potentiometry and in our opinion deserves attention, particularly in those cases where large potential jumps are not observed.

ml of 0.1N $Na_2B_4O_7$

Babko also queries the dissociation constant of boric acid, although the value for this constant is given both in classical textbooks* and in various notebooks**. We find that the value is $K'_{H_2B_4O_7} = 10^{-4}$, i.e. it is equal to the dissociation constants of HCNS, $HNO_2$, etc. Consequently it can be assumed that $H_2B_4O_7$ exists in weak acid solutions.

Babko doubts that we obtained five complexes. Apparently he does not understand that it is only the first two jumps that characterize the formation of iron borate complexes while the other three indicate the progressive decomposition of the complexes with the formation of basic salts; this is confirmed by the results of Table 1 in the article (p.290). From this table it should be clear to any one precisely how the complexes gradually decompose, and how many $BO_2^-$ groups are contained in the basic salts. As regards the first jump on the curve, a similar intermediate jump has also been observed during the titration of aluminum salts with borates, and not only with borates but also with NaF ***. It is incomprehensible why Babko is so hostile to the method we adopted. In each case he does not give any basis for his objections. We have based our conclusions on numerous experimental results and not on some preconceived belief or unbelief in them.

As regards Babko's observations re the simultaneous titraton of $Fe^{3+}$ and $Cu^{2+}$ we have the following to say; if one is to agree with Babko's opinion that during titration with borate, formation of basic salts and of ferric hydroxide occurs, then on titrating a mixture of $Fe^{3+}$ and $Cu^{2+}$, and taking into account the solubility products of the respective hydroxides, $Fe(OH)_3$ should be precipitated first, followed by $Cu(OH)_2$. This is, however, in complete contradiction to experiment, $Cu^{2+}$ is titrated first possibly forming basic salts and $Cu(OH)_2$ (solubility product = $5.6 \cdot 10^{-20}$) while $Fe^{3+}$ is only titrated afterwards with formation of soluble complex compounds.

Moreover, Babko's hypothesis re formation of a colloidal solution of basic salts during the first titration stage of $Fe^{3+}$ ions with borate is impossible, because we observed a similar type of titration not only during titration of aqueous but also of water-alcohol solutions of $Fe^{3+}$ and also of its complex salts, ferric-salicylate, acetate, fluoride, and thiocyanate, respectively. In addition, one may point out for Babko's information that even when obviously colloidal solutions are formed during volumetric reactions, then, in Dumansky's opinion, intermediate complexes are first formed, the composition of which become more complex with time and leads to the formation of products of a colloidal nature.

*I. M. Kolthoff and V. A. Stanger, "Volumetric Analysis", 1, 305 (1950)

**Chemists' Notebook, 3, 493 (1952)

***I. L. Teodorovich, I. Anal. Chem., 7, 175 (1952)

Babko accuses us of not determining the equilibrium concentration of boric acid which is essential for calculation of the instability constants of the complexes. It would be of interest to know why Babko decided that we did not use this value. In our calculations of the instability constants of the complexes we naturally could not but determine the equilibrium concentration of boric acid since the value of the equilibrium concentration is essential for the calculations. We could not, however, put all these calculations in our paper because the amount of material required would be sufficient to fill an article on its own. Moreover, by the very nature of the article as printed, it is the conclusions to be drawn from them and not the calculations as such which are of interest. If the editor is prepared to print the caculations they are welcome to have them at any time.

The cryoscopic method served purely as a confirmation of complex formation during interaction between $Fe^{3+}$ and borate. Babko is rather too insistent about "the neglect of the elementary rules of evaluating the accuracy of results" in which a curve was drawn on the basis of 17 observations. It is necessary to note that the tabulated results are not the results of one experiment but are the means of a whole series of replicate determinations, which is the usual method adopted.

We consider that what we have said above disproves Babko's observations re the nature of the work, and in particular his opinion about the unsuitability of the electrode which we used. Babko's conclusion that the work is of little value occasions surprise, since in his remarks the author subjects to criticism only individual sections of the work and keeps quiet about a number of other important aspects of the work which are very important for an understanding of the nature of the work as a whole.

In passing, we should like to note that at the moment we are studying compounds of a similar type and the results obtained confirm over and over again the participation of $B_4O_7^{2-} \rightleftarrows 2BO_2 \cdot B_2O_3$ in the inner sphere of the complex, equally with other addenda.

Babko's critique is methodolgically incorrect, since it is impossible on the basis of the questions which he has taken up to draw conclusions as to the incorrectness of aspects of the work which he does not understand.

M. B. Shchigol and N. B. Burchinskaya

January 12, 1953

# YU. A. CHERNIKOV

Recently Professor Yu. A. Chernikov, one of the outstanding specialists in analytical chemistry, a Stalin Prize Winner, and a Doctor of Chemical Sciences, celebrated his 60th birthday and the 30th year of his scientific activity.

Chernikov has devoted most of his attention, and still does, to the development of the analytical chemistry of the rare elements. This branch of analytical chemistry is one of the most complex and one of the least studied. The exciting development of industry in the Soviet Union, in particular that of the rare elements constantly requires analysts to develop analytical methods for the raw materials, the manufactured products, and also methods of phase control.

Chernikov during the first years of his scientific activity has strenuously struggled to solve these problems. One of the lines along which he has worked is the development of the theoretical and practical bases for the determination of small amounts of material. For this purpose he has very successfully used colorimetric methods involving the use of various organic reagents such as dithizone, diethyldithiocarbamate, hydroxyquinoline, etc., which ensure the highest sensitivity, accuracy and simplicity. A number of other physico-chemical methods of analysis has been widely developed under his leadership, e.g., internal electrolytical methods, potentiometry, etc.

The methods of analysis developed by Chernikov have been widely used not only in laboratories working on the rare elements but also in ferrous and non-ferrous laboratories.

During his many years in analytical chemistry Chernikov has educated many talented young specialists in this field. His students have defended many theses of great scientific and theoretical interest.

In addition to his scientific work he has also done a large amount of social-scientific service. He is a member of the Commission on Analytical Chemistry of the USSR Academy of Sciences, and a member of the Scientific Society of the Vernadsky Geochemical and Aanlytical Chemistry Institute. He also participates in the work of the J. Anal. Chem.

He was awarded a Stalin Prize in 1947 and the Order of Lenin in 1951 for his work.

The Commission on Analytical Chemistry of the USSR Academy of Sciences and the editorial board of the J. Anal. Chem. hope that Chernikov will be able to continue his successful and fruitful work in the development of analytical chemistry.

# UKRAINIAN CONFERENCE ON CHEMICAL CONTROL IN THE METALLURGICAL AND METAL-WORKING INDUSTRIES

A conference of Ukrainian analytical chemists organized by the Ukrainian branch of the Mendeleev All Union Chemical Society was held at Dnepropetrovsk from the 31st of May to the 4th of June, 1952.

The 277 delegates who attended the conference came from 10 regions of the Ukrainian SSR, from 20 towns – Kiev, Kharkov, Dnepropetrovsk, Stalino, Lvov, Zaporozhe, Krivoi Rog, Voroshilovgrad, Zhdanov, Gorlovka, etc. The delegates represented 72 organizations – 47 factories and 25 scientific research, educational institutions and other organizations. A number of scientific reports devoted to basic chemical control of metal quality was read at the conference.

In Professor A. K. Babko's report (Kiev) on "Colorimetric Methods of Analysis for Control in the Metallurgical Industries" the development of analytical methods in connection with the development of industry and increased demands for improved metal quality was considered.

A. K. Babko clearly demonstrated the prior claims of Russian scientists in the development of colorimetric analytical methods and their application to production control. He gave a brief review of methods of determining contamination in ferrous and non-ferrous metals, and formulated basic problems of further development and introduction of colorimetric methods for metallurgical production.

The necessity of a critical examination of the methods used for determination of silicon and phosphorus in metals and of antimony and arsenic in non-ferrous metals was noted.

S. A. Guskinskaya (Stalin Steel Institute, Moscow) read a report on "The Application of Mathematical Statistics in Analytical Chemistry" in which she explained how to work out results and evaluate them more accurately. She showed by means of many examples that using mathematical statistics it is possible to calculate not only random errors which determine reproducibility, but also the deviation of results of individual determinations, and to establish the presence of systematic errors which determine the correctness of the analysis.

S. A. Guskinskaya gave suitable formulas and tables for getting results by the treatment of only a relatively small number of observations which characterize the observed phenomena to the same accuracy as the more complex classical methods of mathematical statistics used hitherto

V. S. Rossikhina and I. L. Tsykory (Dnepropetrovsk State University) in their report on "An Experiment on the Application of Spectral Methods for the Analysis of Materials, Slags and Ores" showed considerable success in developing spectral methods in the USSR and its application to production control.

The report dealt with work carried out at Dnepropetrovsk State University on attempts at introducing methods of quantitative spectral analysis into the work of factory laboratories in the Dnepropetrovsk and Zaporozhe areas. A spectrographic method has been developed by the authors for the analysis of copper, iron, manganese, magnesium, and silicon in aluminum alloys. Spectrographic methods for the analysis of rustless steel, iron ore, slag, etc., were also given. All the methods were tested on apparatus of Russian make and have been successfully introduced into production.

Engineers E. A. Nechaeva and O. Ya. Orlova (Petrovsk Metallurgical Factory, Dnepropetrovsk) read a paper on "The Determination of Non-Metallic (Slag) Inclusions in Ferrous Metals" which included a description of an improved method for studying non-metallic inclusions. In the improved method the apparatus which is used for the individual separation of the unstable manganese compounds in the anode residues is modified. The method for the removal of ferric oxide was also improved. Photocolorimetric methods were used for the determination of the chemical compositions of a whole series of stable non-metallic inclusions. The importance of petrographic methods for the study of non-metallic inclusions in metals was demonstrated, as well as the advantages of spectrographic methods in combatting flaws in metal ingots and in finished metal products.

Gurevich (Ukrainian Institute of Metals, Kharkov) in his report on "Chemical Methods for the Determination of Non-Metallic Inclusions and Gases in Carbon Steels", stated that electrolytic methods are the most complete and reliable methods for the separation of metallic and non-metallic phases. The author dealt with

of inclusions of manganese oxide, the removal of sulfur inclusions in manganese and iron, the removal of ferrous oxide from electrolyte residues, and the determination of non-metallic inclusions stable in dilute HCl. The authors suggested a method for the removal of non-metallic inclusions from carbon steels based on lowering the acidity of the electrolytic bath used for electrolysis.

Yu. I. Usatenko and engineers E. L. Grenberg and V. L. Kopelovich in their report on "Photocolorimetric Determination of Aluminum in Steel with "Stilbazo" without Preliminary Removal of Iron" gave details of the method they used for the photocolorimetric determination of aluminum using a new reagent "Stilbazo" synthesized by Soviet chemists. The method has a very great advantage, viz., the possibility of determining aluminum in the presence of many other elements. The method has been introduced into factory practice.

Reports were read by workers of the analytical section of the Dnepropetrovsk State University on the application of photocolorimetry to metal and ore analysis.

V. I. Reznik dealt with the use of phototurbidimetric titration for the analysis of dolomites and limestones and to the study of the precipitation reactions of magnesium, calcium, aluminum, iron and other metals.

V. D. Vasilenko devoted his paper to the application of photocolorimetric methods to the "non-destructive" analysis of metals and proposed a method of this type for the determination of manganese in carbon steels, and low alloy steels and casts. He also proposed a method for the determination of iron in copper and aluminum alloys. The experimental results were compared with results of spectrographic and gravimetric methods and also with specification tests and gave satisfactory agreement.

L. S. Sedyuk suggested a method for the determination of nickel and cobalt in manganese ores – a problem of considerable interest at present. Nickel determination is based on its separation from manganese by internal electrolysis with subsequent photocolorimetric determination with dimethylglyoxime in alkaline media, while cobalt is determined with nitroso-R-salt.

V. F. Maltsev and V. Ya. Sych (Tube Institute, Dnepropetrovsk) in their paper on "A Rapid Electrolytic method for testing steel for intercrystalline corrosion," critically examined existing methods of determining intercrystalline corrosion and proposed a new, rapid method for its determination.

The following papers were also read: –

"Rapid Analysis of Martensite and Foundry Slag". (F. G. Druzhinin-Stalin Metallugical Factory, Stalino); "Photocolorimetric Determination of Chromium in Slag". (V. A. Begma and V. I. Zhuravskaya-Karl Liebknecht Factory, Dnepropetrovsk). "A Rapid Method of Estimating Manganese in Ferromanganese and in Manganese Ores". (A. P. Belyaeva-Petrov Factory, Dnepropetrovsk), "Determination of Lead by Internal Electrolysis Using an Aluminum Anode". (B. Ya. Barko, Dnepropetrovsk); "The Application of Ionites (Ion Exchange Resins) for the Determination of Boron in Alloys and Certain Electrolytes", (Ya. A. Degtyarenko, Lvov Polytechnic Institute]. "Determination of Slag Basicity by Means of Basicity Meters", (S. M. Tarashchanskaya, Voroshilovgrad) "Oxidation of Manganate to Permanganate by Persulfate without Using $AgNO_3$", (I. M. Malkin, Dnepropetrovsk Metallurgical Institute; " Some Analytical Properties of di-Betanaphthylthiocarbazone and its application for the Determination of Zinc and Iron Ores", (A. S. Grzhegorzhevsky, Dnepropetrovsk Metallurgical Institute). "Metallic Iron in Laboratory Tests for Ores and Other Materials", (N. S. Tkachenko Krivoi Rog "Gikyuzhruda") "Organization of Work in the "Red Star, Factory Chemical Laboratory". (M. G. Berdynskaya Kirovograd).

21 papers were read in all at the confernce, 10 of the papers by factory representatives and 11 by members of Scientific Research Institutes.

The conference established that Soviet analytical chemists have achieved considerable successes in organizing work in factory chemical laboratories, and in introducing advanced physico-chemical and physical methods of production control.

New gravimetric volumetric, colorimetric and other methods have been developed by various institutes, factories, and mining laboratories which can be widely used in practice.

At the end of the conference the participants unanimously adopted a resolution in which detailed recommendations were given for further improvements in analytical laboratories. The successful realization of the resolutions of the conference must be carried out by all analytical chemists in factories and institutes of the Soviet Ukraine, who can contribute greatly to the fulfilment of Comrade Stalin's plans for building a communist society.

1. 1,4-Ethylbenzylaminophenylmercury cyanide.

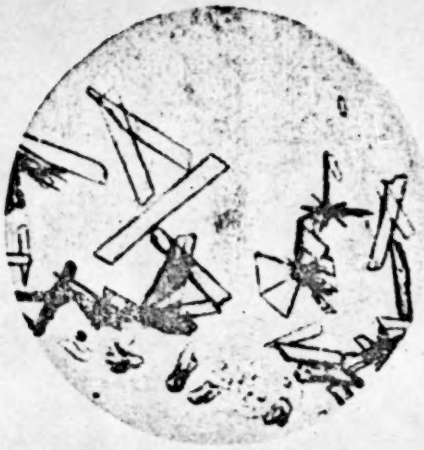


Fig. 2. Reagent – 1,4-ethylbenzylaminophenylmercuryacetate.

Fig. 3. 1,4-Dimethylaminophenylmercury-cyanide (in aqueous solution).

4. 1,4-Dimethylaminophenylmercury-cyanide (in acetic acid solution)

Fig. 5. Reagent – 1,4-Dimethylaminophenylmercury acetate.

Fig. 6. 1,2-Toluidine-4,6-dimercury-cyanide.

7. Reagent – 1,2-Toluidine-4,6-dimercury acetate.

Thermal Analysis with Registration of the Volume of Gas Evolved (page 171)

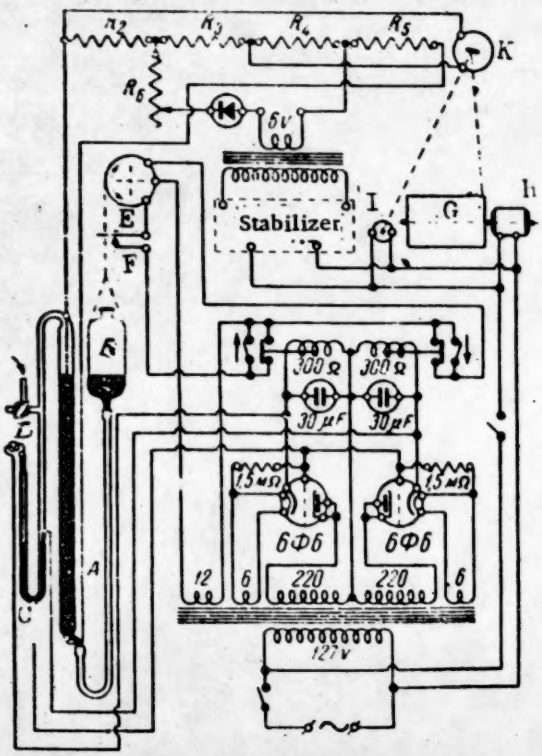



Fig. 1.

# ENGLISH TRANSLATIONS OF RUSSIAN CHEMICAL JOURNALS.

CONSULTANTS BUREAU publishes complete English translations of the following major Russian chemical journals, on a yearly subscription basis:

JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR
Six issues per year. Translation began with Vol. VII (1952) ... ... ... $80.00 per year

JOURNAL OF APPLIED CHEMISTRY OF THE USSR
Twelve issues per year. Translations began with Vol. XXIII (1950) ... $80.00 per year

JOURNAL OF GENERAL CHEMISTRY OF THE USSR
Twelve issues per year. Translation began with Vol. XIX (1949) ... ... $95.00 per year

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OF CHEMICAL SCIENCE
Six issues per year. Translation began with the 1952 volume ... ... ... $80.00 per year

COLLOID JOURNAL (USSR)
Six issues per year. Translation began with Vol. XIV (1952) ... ... ... $80.00 per year

*The subscription price includes cross index to each volume of the English translation. All tabular material, diagrams, photographs, etc., accurately reproduced. Translation is cover-to-cover. Each issue is mailed to subscribers upon publication.*

COMPLETE TRANSLATION OF ANY SINGLE PAPER
FROM ANY OF THE ABOVE LISTED JOURNALS ... $7.50

## *INDIVIDUAL TRANSLATIONS OF ANY TECHNICAL MATERIAL— TO OR FROM ANY LANGUAGE:*

Accurate, intelligent, knowing interpretation of the original paper into idiomatic English, by bilingual specialists in all technical and scientific fields. Prompt service. Exceptionally low rates, made possible by our large-scale translation publishing program.

from { FRENCH, GERMAN, RUSSIAN, SPANISH } to English, only ... ... $10.00 per 1000 words

*other rates upon request*

CONSULTANTS BUREAU, 152 West 42nd Street, New York 18, N.Y.